

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244570406>

Preparation and photoelectron spectrum of the CH₃I⁻ anion: Rare gas cluster mediated synthesis of an ion-radical complex

ARTICLE in JOURNAL OF THE AMERICAN SOCIETY FOR MASS SPECTROMETRY · SEPTEMBER 1999

Impact Factor: 2.95 · DOI: 10.1016/S1044-0305(99)00057-4

CITATIONS

15

READS

26

6 AUTHORS, INCLUDING:



Steen Brøndsted Nielsen

Aarhus University

197 PUBLICATIONS 3,072 CITATIONS

SEE PROFILE

Preparation and Photoelectron Spectrum of the CH_3I^- Anion: Rare Gas Cluster Mediated Synthesis of an Ion–Radical Complex

Jun Kim,^{*} Jude A. Kelley,^{*} Patrick Ayotte, Steen B. Nielsen,[†]
Gary H. Weddle,[‡] and Mark A. Johnson[†]

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, USA

We report the preparation of the bare and argon-solvated anion of CH_3I , and characterize this species using negative ion photoelectron spectroscopy at 3.495 eV. The photoelectron spectrum consists of a narrow band appearing 0.11 ± 0.02 eV above the binding energy of isolated iodide. Such behavior is similar to that displayed by iodide-(closed shell) solvent molecule complexes, indicating that photodetachment does not access the bound region of the CH_3I potential. These observations suggest that CH_3I^- rearranges (after electron capture) to an ion–radical complex. We advance the hypothesis that this complex adopts a C_{2v} structure where the ion is hydrogen bonded to the methyl radical. (J Am Soc Mass Spectrom 1999, 10, 810–814) © 1999 American Society for Mass Spectrometry

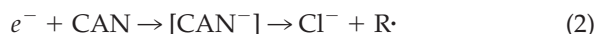
Dissociative electron attachment (DA) onto methyl iodide:



is an archetypal example (along with SF_6) of the diabatic capture of very slow electrons [1–5]. This propensity arises because of the potential energy curves sketched in Figure 1, where the repulsive anionic curve “intersects” the neutral very close to its equilibrium separation [6]. The process of DA therefore occurs without a barrier (for s waves) at low electron collision energies, providing ion chemists with a very efficient means for iodide production in a variety of ion sources. At short range, the $\text{CH}_3\text{--I}^-$ interaction is quite repulsive because the closed shell I^- ion cannot form a covalent bond with the CH_3 radical. In fact, it is generally assumed by most researchers that CH_3I^- is unstable in isolation, a view supported by several recent theoretical reports which conclude that the CH_3I^- system does not support a bound state [7, 8]. Here we are concerned with the form of the CH_3I^- anionic potential at large C–I distances, and in particular whether this potential can support a weakly bound or metastable negative ion in analogy with the recent observation of isolated HI^- by Carman

et al. [9], where the excess charge is localized on iodide tethered to a distant hydrogen atom [10]. In this article, we report the successful synthesis and characterization of anionic methyl iodide, CH_3I^- .

The halide-based, $\text{X}^- \cdot (\text{R}\cdot)$ class of ion–radical complexes relevant to the present discussion is reminiscent of the halide ion–carbenes discovered by Paulino and Squires [11], and indeed this study was motivated by their work. Gas phase ion–radical complexes are relatively rare, with the 2-chloroacrylonitrile [CAN] anion $\text{Cl}^- \cdot (\text{CH}_2\text{CCN}\cdot)$ having been reported earlier from our laboratory [12]. The photoelectron spectrum of CAN^- appears as a narrow band shifted by about 0.88 eV above the electron binding energy of bare Cl^- , confirming its identification as an ion–radical complex (note that the $\text{Cl}^- \cdot \text{CAN}$ ion–molecule complex is shifted by 0.80 eV [12]). Calculations [13] confirm that CAN ($\text{CH}_2=\text{CCNCl}$) undergoes massive rearrangement upon electron attachment, where the nascent Cl^- ion migrates around to the methylenic end of the $\text{CH}_2=\text{CCN}$ radical fragment and binds to the hydrogen atom *trans* to the cyano group. The driving force for this rearrangement is apparently the ion–dipole interaction, where the chloride ion is initially formed on the negative end of $\text{CH}_2=\text{CCN}$. Migration toward the positive end of the dipole leads to an exposed radical center in a distonic (charge and radical separated [14, 15]) complex. In the CAN case, dissociative electron attachment:



is nearly thermoneutral, so that the unstable CAN^- ion can be observed as a long-lived metastable species, even

Address reprint requests to Prof. Johnson, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520-8107. E-mail: mark.johnson@yale.edu

^{*} These authors contributed equally to this work.

[†] Present address: Department of Chemistry, University of Copenhagen, The H.C. Ørsted Institute, DK-2100 København Ø, Denmark.

[‡] Present address: Department of Chemistry, Fairfield University, Fairfield, CT 06430.

Dedicated to the memory of Professor Robert Squires.

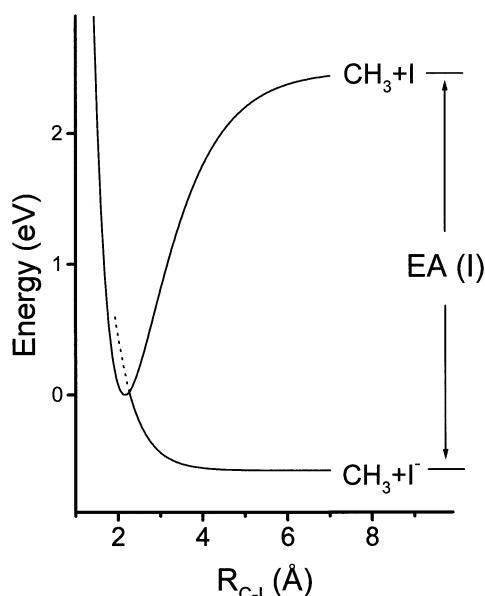
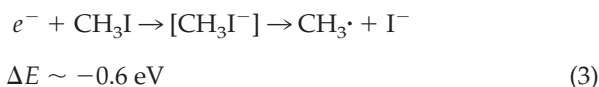


Figure 1. Schematic potential energy curves for neutral and anionic CH_3I along the C–I stretching coordinate.

when electron attachment occurs in an isolated collision [Tsukuda and Kondow, private communication].

The CH_3I^- synthesis is much more challenging than that of CAN^- because its prompt, impulsive dissociation upon electron attachment:



is, in fact, at the heart of the well known nonstatistical dynamics displayed by harpoon reactions [16]. This recoil energy is largely channeled into translational energy of the lighter methyl fragment, and the lifetime of the $[\text{CH}_3\text{I}^-]$ transient negative ion is so short that it is very difficult to stabilize (by three-body interactions, for example) prior to dissociation. Synthesis of a putative CH_3I^- species via the stabilization of the reverse reaction intermediate in eq 3 is clearly unattractive as it would require a source of methyl radicals. As a result, no negatively charged alkyl iodides have been observed in the gas phase (although there is a report of a transient identified as CH_3I^- which appeared upon photoionization of CH_3I in a free jet [6]).

Nonetheless, CH_3I^- and several other RX^- species have been observed in rare gas matrices [17], where the recoil energy is presumably accommodated by caging of the nascent fragments in the rare gas host. Their EPR spectra indicate that they are basically $\text{X}^- \cdot (\text{R}\cdot)$ ion-radical complexes with most unpaired spin density on the carbon atom. In this paper we exploit a cluster variation of this matrix isolation method, and report the formation of bare and solvated CH_3I^- , synthesized using argon clusters as the host medium. We then

characterize the chemical nature of this species using negative ion photoelectron spectroscopy.

Experimental

Our negative ion source [18] consists of a high energy (1 keV) electron beam ionizing a pulsed supersonic expansion at the high density region near the nozzle. Secondary electrons are trapped, cooled in the free jet, and then attach to species seeded in the argon carrier gas. Here we use only a trace amount of CH_3I in about 3 atm of argon, where CH_3I vapor is flooded into the manifold behind the nozzle, completely evacuated with a mechanical pump, and then filled with pure argon. The ions drift about 15 cm in the source before being pulsed into a tandem time-of-flight negative ion photoelectron spectrometer described previously [18]. Briefly, this spectrometer uses field-free, time-of-flight for electron kinetic energy analysis. Photodetachment was carried out with the third harmonic from a Nd:YAG (Spectra Physics GCR-4) laser, and the spectrum results from the accumulation of photoelectrons from 50,000 laser shots.

Results and Discussion

The $\text{CH}_3\text{I}^- \cdot \text{Ar}_m$ ($0 \leq m \leq 11$) Cluster Distributions: Observation of the Bare CH_3I^- Ion

Mass spectra from the jet ion source are displayed in Figure 2. The resolution of the mass selection stage is greater than 500 in the neighborhood of 142 u, enabling us to definitively identify CH_3I^- in the spectrum (141.93 vs. 141.88 u for experimental and calculated values of the CH_3I mass, obtained by calibration with the nearby $\text{I}^- \cdot \text{H}_2\text{O}$ peak. The latter was unambiguously identified through its vibrational spectrum). The most intense peaks in the cluster distribution (Figure 2) are due to $\text{I}^- \cdot \text{Ar}_n$ clusters, whereas the weaker interloper peaks correspond to incorporation of 15 u onto the $\text{I}^- \cdot \text{Ar}_n$ clusters, as expected for the CH_3I^- -based clusters. Note that the bare CH_3I^- ion is efficiently produced, suggesting that this species indeed possesses either a bound or long-lived metastable state.

We have studied the collision-induced decay behavior of the CH_3I^- peak, and found significant loss of 15 u, verifying that it indeed possesses an iodine atom. The intensity of the CH_3I^- progression was found to be extremely sensitive to the exact location of the ionizing electron beam relative to the nozzle orifice, and the upper trace in Figure 2 illustrates how the distribution changes when the source is tuned to enhance the formation of large clusters. Interestingly, the $\text{CH}_3\text{I}^- \cdot \text{Ar}_m$ distribution is *inverted* in the sense that it displays a local maximum with 6–7 argon atoms. The bare CH_3I^- peak was always found to be accompanied by the argon distribution, indicating that the argon clusters are intrinsic to its formation. (Note that bare CH_3I^- was produced under the conditions which yield the upper

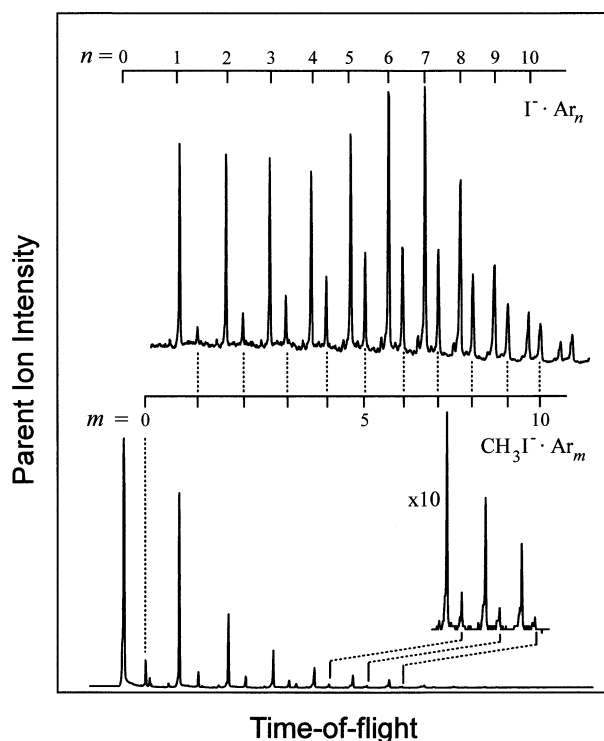


Figure 2. Mass spectrum from the electron impact ionized free jet ion source, illustrating the formation of $\text{CH}_3\text{I}^- \cdot \text{Ar}_m$ clusters at two different conditions (see text). Note their enhanced formation in the range $m = 6$ – 7 in upper trace.

trace in Figure 2, with an intensity expected by extrapolating the behavior of the larger clusters, but was artificially cut off by our time-of-flight observation window.) We will consider the dynamics of the argon mediated synthesis in a following section.

Photoelectron Spectrum and Qualitative Implications on the Structure of CH_3I^-

Figure 3 presents the 3.495 eV photoelectron spectrum of the CH_3I^- ion, in addition to the spectrum of bare I^- for comparison. The ion was prepared under the source condition which yields the mass spectrum displayed in the lower trace in Figure 2. The CH_3I^- peak is shifted $0.11 (\pm 0.02)$ eV higher in binding energy relative to the bare I^- feature (lower trace in Figure 3), and is quite narrow (FWHM 17 and 50 meV for I^- and CH_3I^- , respectively). Note that, neglecting the binding energy of the anion (which is expected to be very small, if indeed nonzero) the adiabatic electron binding energy (denoted AEA in Figure 3b) is on the order of only 0.6 eV or so. Thus, the observed peak lies far above the adiabatic origin of the photoelectron spectrum.

The shift to higher energy has qualitative implications on the nature of this anion. Inspection of the potential curves sketched in Figure 1 indicates that even for very large excursions of the C–I bond length (in C_{3v}

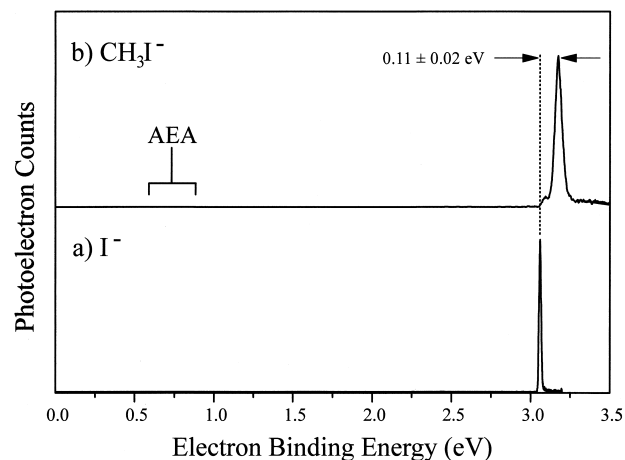
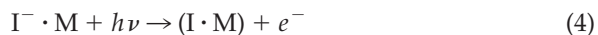


Figure 3. Photoelectron spectrum (3.495 eV) of (a) I^- and (b) CH_3I^- . AEA indicates the range of the adiabatic electron affinity (the uncertainty being the binding energy of the anion). Note that the observed band lies far above the true vibronic origin.

symmetry), we would generally expect a broad photoelectron band, displaced lower in binding energy than that of I^- (3.06 eV), as photodetachment accesses the attractive region of the CH_3I curve and launches high amplitude vibration along the C–I stretching coordinate. If the C–I distance is so great in the anion that only the flat region of the long range C_{3v} potential is accessed in detachment, the observed 0.11 eV increase in binding energy over that of I^- must be associated with the anion. Such strong binding is difficult to reconcile with a very long C–I bond length, especially when calculations indicate that system is not likely to even possess a minimum [7, 8]!

The CH_3I^- photoelectron band is actually reminiscent of the spectra arising from complexation of halides with closed shell molecules (i.e., CH_3CN [19]) where the increased electron affinity of the complex (above that of I) arises when the strong binding in the ionic complex is not compensated in the more weakly interacting, neutral radical–molecule complex:



The narrowness and position of the CH_3I^- band similarly indicate that photodetachment of the (charge-localized) $\text{I}^- \cdot (\text{CH}_3\cdot)$ complex occurs to a very weakly bound or even locally repulsive region of the I– CH_3 surface, ruling out C_{3v} symmetry for the anion. We note that we have also obtained the photoelectron spectrum of the argon-solvated $\text{CH}_3\text{I}^- \cdot \text{Ar}$ cluster, and find a similarly narrow feature displaced ~ 25 meV above the band in the bare CH_3I^- complex. This shift is quantitatively similar to that found by Yourshaw and co-workers [20] for the argon shifts in the $\text{I}^- \cdot \text{Ar}_n$ clusters (27 meV for the first Ar), further indicating that CH_3I^- is composed of a charge localized, iodide core ion.

Assignment of the Ion–Radical Structure with Empirical Evidence and Ab Initio Calculations

These considerations point to substantial rearrangement in the CH_3I^- anion to an $\text{I}^- \cdot (\text{CH}_3\cdot)$ ion–radical complex with a structure far from the C_{3v} symmetry of the neutral. We therefore entertained the possibility that, like the CAN^- system discussed in the Introduction, the ion binds to a hydrogen in the methyl radical. This C_{2v} symmetry (i.e., planar $\text{I}^- \cdot \text{HCH}_2$) structure would readily explain the qualitative features of the observed photoelectron spectrum (Figure 3). Photodetachment from such an arrangement generates the $\text{I} \cdot \text{HCH}_2$ biradical very far from the deep attractive C_{3v} well of the neutral molecule, in a region more typical for photodetachment of I^- near a closed shell neutral molecule. Furthermore, we expect this to be a flat region of the neutral surface because the vibrational wave packet would be launched with methyl on the plateau between the two valleys corresponding to bond formation to the open p orbital on sp^2 hybridized carbon.

The C_{2v} hypothesis does not appear to have been considered in the literature, and we therefore challenged it using ab initio calculations [21] on the simpler $\text{Cl}^- \cdot \text{HCH}_2$ system, which should display the same binding characteristics if the dominant interaction arises from ion–induced dipole forces. At the MP2/6-31G** level of theory, we indeed find that the C_{3v} structure is unstable with respect to dissociation, but interestingly, is locally stable at fixed C–Cl distance with respect to tipping the C_3 axis of the methyl away from the C–Cl bond axis. The system does display a true (at least local) minimum structure, however, in C_{2v} symmetry ($\text{Cl}^- \cdot \text{HCH}_2$). This structure appears to be aided both by the formation of a hydrogen bond and the polarizability associated with distortion of the planar CH_3 species along the E symmetry scissors mode.

Photodetachment of an $\text{I}^- \cdot \text{HCH}_2$, C_{2v} complex, creates an interesting $\text{I}(^2P_{3/2}) + \text{CH}_3(^2A'')$ neutral biradical. Far apart, we expect weakly bonding and antibonding molecular orbitals to arise from the three p orbitals on iodine and the p orbital on carbon, resulting in a complex manifold of closely spaced singlet and triplet configurations. It is presently unclear whether some or all of the resulting electronic states display local minima in the C_{2v} form, although qualitatively it seems that there should be one preferred π bond between the two parallel (out of plane) p orbitals. In any event, further calculations on this interesting biradical species should be both challenging and informative. In particular, if some of the neutral configurations are locally stable, their preparation via photodetachment of $\text{I}^- \cdot \text{HCH}_2$ would provide a unique opportunity to explore this very high energy isomer of methyl iodide.

Remarks on the Cluster-Mediated Synthesis

The formation of CH_3I^- requires quenching the substantial recoil energy released upon electron attachment

(eq 3). The kinematics of this process indicate that most of the kinetic energy is imparted to methyl, and this, in turn, requires that methyl iodide is either encapsulated within a large argon cluster, or that the methyl end is selectively pointing into the argon cluster where its kinetic energy can be dissipated. A similar suppression of the hydrogen atom kinetic energy release was recently observed by Garciavela and co-workers [22] in the argon cluster mediated photodissociation of HCl. A similar cluster-mediated suppression of recoil fragmentation in the dissociative attachment was also recently reported in the NF_3/Ar system [23].

One important clue about the formation mechanism lies in the cluster distributions displayed in Figure 2, where we observed that a significant amount of the iodine-containing clusters retain the methyl, and that this fraction increases with increasing cluster size (upper trace in Figure 2). The inverted nature of the $\text{CH}_3\text{I}^- \cdot \text{Ar}_m$ distribution points to enhancement of methyl retention and hence increased caging of the nascent fragments in the larger neutral precursor clusters, leading to kinetically stable ionic clusters containing six or seven argon atoms. Because we expect that about 0.75 eV of energy is released upon attachment (0.6 eV in recoil and ~ 0.15 eV from solvation of the iodide moiety [20]), about 12 argon atoms are ejected in evaporative cooling of the nascent complex. Thus, the neutral precursor contains on the order of 18 argon atoms, the same range where Yourshaw and co-workers [20] find evidence for completion of an argon solvent shell around I^- . The fact that significant caging occurs for much smaller clusters indicates that the methyl preferentially points into the argon subcluster at smaller sizes.

Summary

The CH_3I^- anion has been prepared using electron attachment to methyl iodide in 10–20 atom argon clusters. The photoelectron spectrum of this ion appears strikingly similar to that characteristic of iodide-(closed shell) molecule complexes, indicating that photodetachment does not access the bound region of the CH_3I potential. We explain these observations with the hypothesis, supported by ab initio theory, that the ion–radical complex adopts (planar) C_{2v} geometry with the open carbon p orbital pointing out of the plane.

Acknowledgments

We thank the National Science Foundation, Chemistry Division, for generous support of this work. PA acknowledges support from FCAR (Québec), and GHW thanks Fairfield University for a sabbatical fellowship.

References

1. Ziesel, J. P.; Nenner, I.; Schulz, G. J. *J. Chem. Phys.* **1975**, *63*, 1943.
2. Christophorou, L. G. In *Advances in Electronics and Electron Physics*; Academic: New York, 1978; Vol. 46, p 55.

3. Stockdale, J. A. D.; Davis, F. J.; Compton, R. N.; Klots, C. E. *J. Chem. Phys.* **1974**, 60, 4279.
4. Alajajian, S. H.; Bernius, M. T.; Chutjian, A. *J. Phys. B* **1988**, 21, 4021.
5. Klar, D.; Ruf, M.-W.; Hotop, H. *Chem. Phys. Lett.* **1992**, 189, 448.
6. Chupka, W. A.; Woodard, A. M.; Colson, S. D. *J. Chem. Phys.* **1985**, 11, 4880.
7. Modelli, A.; Scangnolari, F.; Distefano, G.; Jones, D.; Guerra, M. *J. Chem. Phys.* **1992**, 96, 2061.
8. Nagesha, K.; Marathe, V. R.; Krishnakumar, E. *Int. J. Mass Spectrom. Ion. Processes* **1995**, 145, 89.
9. Carman, H. S., Jr.; Klots, C. E.; Compton, R. N. *J. Chem. Phys.* **1993**, 99, 1734.
10. Schwerdfeger, P.; Szentpaly, L. V.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, 87, 510.
11. Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, 113, 1845.
12. Dessent, C. E. H.; Bailey, C. G.; Johnson, M. A. *Chem. Phys. Lett.* **1995**, 244, 127.
13. Riveros, J. M.; Breda, A. C.; Blair, L. K. *J. Am. Chem. Soc.* **1973**, 95, 4066.
14. Stirk, K. M.; Kiminkinen, L. K. M.; Kenttamaa, H. I. *Chem. Rev.* **1992**, 92, 1649.
15. Guo Y.; Grabowski, J. J. *J. Am. Chem. Soc.* **1991**, 113, 5923.
16. Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1967**, 55, 233.
17. Raynor, J. B.; Rowland, I. J.; Symons, M. C. R. *J. Chem. Soc. Faraday Trans.* **1991**, 87, 571.
18. Johnson, M. A.; Lineberger, W. C. In *Techniques for the Study of Gas-phase Ion Molecule Reactions*; Farrar, J. M.; Saunders, W., Eds; Wiley: New York, 1988; p 591.
19. Dessent, C. E. H.; Bailey, C. G.; Johnson, M. A. *J. Chem. Phys.* **1995**, 103, 2006.
20. Yourshaw, I.; Zhao, Y. X.; Neumark, D. M. *J. Chem. Phys.* **1996**, 105, 351.
21. GAUSSIAN 94, Revision E.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1995.
22. Garciavela, A.; Gerber, R. B.; Buck, U. *J. Phys. Chem.* **1994**, 98, 3518.
23. Ruckhaberle, N.; Lehmann, L.; Matejcik, S.; Illenberger, E.; Bouteiller, Y.; Periquet, V.; Museur, L.; Desfrancois, C.; Schermann, J.-P. *J. Phys. Chem.* **1997**, 101, 9942.