Rapid bond rearrangement in molecules after core-electron excitation

S L Sorensen, M Gisselbrecht, J Laksman¹, E P Månsson, D. Céolin², A Sankari
Department of Physics, Lund University, Box 118, 22100 Lund, Sweden

F Afaneh
The Hashemite University, Box 150459, Zarqa, 13115 Amman, Jordan
E-mail: stacey.sorensen@sljus.lu.se

Abstract. Experimental studies of core-excited molecules using three-dimensional multi particle momentum imaging are presented where bond rearrangement processes in dication species are analysed. The aim of the study is to understand the relation between the geometric changes associated with core-excited states and the kinetic energy released in particular molecular dissociation processes. The kinematics of individual fragmentation channels are studied by fully three-dimensional momentum imaging of fragments in coincidence. Examples are presented where the high efficiency of the instrument and the fully three-dimensional momentum capabilities are exploited to understand nuclear motion leading to bond rearrangement in core-excited states. We identify bond-rearrangement processes in water, carbonyl sulphide and acetylene which are initiated in the core-excited state. In water this is evidenced by the H⁺₂/O⁺ ion pair, and in carbonyl sulphide the OS⁺⁺C⁺ pair is the fingerprint of this reaction. In acetylene the H⁺₂ + C⁺₂ ion pair indicates a molecular geometry that changes from linear to strongly bent. We measure the angular distribution of all fragments and fragment pairs and for the bond rearrangement processes in water and in core-excited acetylene the angular distribution of fragments suggests that the bond rearrangement is very rapid.

1. Introduction

New experimental techniques based upon powerful multi coincidence spectroscopies with fully three-dimensional momentum information are driving new developments in many branches of atomic and molecular physics[1]. One application is the study of dynamics in molecules where geometric information and information on the internal energy of larger molecular systems are essential. Experiments that aim for complete three-dimensional detection of particles from dissociative photoionization show promise for a broad understanding of ionisation dynamics[2]. While this method is very well suited to small molecules where a detailed kinematic picture is obtained a more comprehensive picture of kinematics can also be obtained in large molecules and clusters. Proton migration in molecules is an essential step in the formation of chemical bonds. Proton momentum measurements can be used to identify key isomerization processes,

¹ Present address: MAX-Lab, Lund University, Box 118, Lund 221 00, Sweden
² Present address: Synchrotron SOLEIL, L’Orme des Merisiers, St. Aubin BP 48, F-91192 Gif-Sur-Yvette, France
unravel fragmentation mechanisms and to obtain dissociation lifetimes. Water and acetylene are ideal candidates for such studies using core-electron excitation since they are well studied using electron and absorption spectroscopies and the lowest unoccupied molecular orbitals in both molecules have interesting properties. This study focuses primarily on the dissociation of dication species where two ionic fragments are created and the energetics of the dissociation can be probed using multi coincidence ion imaging spectroscopy. The aim is to understand the role of the core-electron excited state in the bond rearrangement process. In acetylene and in water bond rearrangement has been identified previously although most studies are on cation species. In acetylene there are several energetically favorable paths predicted to lead to a vinylidene geometry [3, 4], and Palaudoux predicted another path via a bridged geometry transition state [5]. Thissen [6] measured the threshold for rearrangement to vinylidene in the dication after photoexcitation around 34 eV. In the core-excited state Gadea et al. discussed the implications of fast proton migration in a theoretical study of acetylene [7] and Osipov measured a proton migration time of about 60 fs for ionisation via this state [8] in accord with the time scale found in laser pump-probe studies in the inner-valence region [9]. Jiang found a 51 fs proton migration time for the acetylene to vinylidene isomerization process in a pump-probe study using the FLASH free-electron laser [10].

Nuclear dynamics in water has been studied for more than 60 years, although most studies focus upon singly-ionised species. In 1940 Mann detected the hydrogen molecular ion after valence electron ionisation in an early study [11] but the most thorough studies of bond rearrangement in water have been made using proton impact (see, for example Ben-Itzhak [12]). Eland studied double ionisation in water and reported evidence for an O$^+$ + H$_2^+$ ion-pair channel in the two-electron spectrum [13] which was confirmed in an ion-ion coincidence study by Tan [14].

The 4a$_1$ state in water is known to be highly repulsive and dissociation of the molecule in the core-excited state (i.e. on the time scale of the 3 fs electronic life time) [15]. Rajgara et al. measured H$_2^+$ fragments after fs pulsed laser excitation, and surmised that the rearrangement process originates in the dication [16]. Ion fragment yield spectra measured near the O 1s threshold found the hydrogen molecular ion and Hiraya connected the vibrational progressions to the ion yield at the O 1$s^{-1}2b_2$ core-excited state thus confirming the role of the core-excited state in the H$_2^+$ formation [17].

Another example that will be presented here is core-excited carbonyl sulphide. Bond rearrangement in OCS is identified in conjunction with the Renner-Teller split core-excited state [29], despite the fact that OCS has no light atoms.

In the three examples shown here we discuss the angular distribution of fragment pairs measured after resonant excitation of core electrons. The angular distribution is determined primarily by the dipole-interaction between light with linear polarisation and the molecule in the resonant transition. Molecules with a favourable orientation among an ensemble of randomly-oriented molecules will be excited with a higher probability. The experimental apparatus and data acquisition are described briefly in the following section.

2. Experiment
The measurements were performed at the soft X-ray undulator beamline I411 at MAX-lab in Lund, Sweden [18]. An imaging time-of-flight spectrometer designed for full 4π transmission for ions up to about 20 eV is used to measure the momenta of ions in three dimensions [19]. The spectrometer has a two-stage acceleration with an electrostatic lens for optimal ion focussing to large-area position-sensitive detector (ROENTDEK DLD80). The spectrometer time-of-flight axis is mutually perpendicular to the polarization vector of the X rays and to the propagation direction of the synchrotron light. The sample is introduced via an effusive gas jet for all of the studies presented here.
Figure 1. The kinetic energy imparted to the fragments originates on the potential energy surface of the dication after the system dissociates the excess energy is shared between the fragments. The photo excitation to the core-excited neutral state is made within the Franck-Condon region and prepares the intermediate state which subsequently decays via Auger emission in one or more steps. The photon energy can be tuned with the limits defined by the Franck-Condon region.

The timing data are transformed into a three-dimensional momentum space. Data subsets are extracted by filtering by criteria for angle, mass, momentum or by coincidence criteria. In the analysis we assume the validity of the axial-recoil approximation and the anisotropy of the ejected fragment ions is directly related to the angle between the molecular transition dipole moment and the fragment ejection. Ionic fragments ejected with higher kinetic energy have been shown to fulfill this condition very well.

In the determination of the molecular anisotropy parameter $\beta$ the photoionisation cross section for a resonant transition between the ground state and a core-electron excited state with a well-defined symmetry is the starting point. The conventional expression for the differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)]$$

where $\sigma$ is the total cross section (integrated over all angles), $\theta$ is the angle between the molecular bond and the polarization direction and $P_2$ is the second-order Legendre polynomial, $P_2(x) = (3x^2 - 1)/2$.

For our setup the intensity can be assumed to be symmetric about the polarisation vector, and reflection symmetry in the plane containing the polarisation vector and the spectrometer axis. The geometry of setup is shown schematically in Fig. 2.

Since fragment intensities have cylindrical symmetry about $\vec{\varepsilon}$ we consider only the polar angle distribution $I(\theta)$. Integration over the azimuthal angle $\phi$ using $d\Omega = \sin \theta d\theta d\phi$ gives

$$I(\theta) = \frac{d\sigma}{2} \sin \theta [1 + \beta P_2(\cos \theta)].$$

A value for $\beta$ can be extracted from a fit of this function to the experimental angular distribution. Possible sources of systematic error include non-uniform detector efficiency, incorrect detector coordinates and uncertainties in the direction of the polarization vector, $\vec{\varepsilon}$.
Figure 2. Schematic drawing of the geometry of the experiment showing the relevant angles for the anisotropy measurement. The plane-polarised synchrotron radiation propagates in a direction orthogonal to the direction of the spectrometer axis and to the polarisation vector. The electron detector which provides a start signal is not shown but the ion time of flight and the trajectories of ions moving towards the detector are included in the sketch.

We shifted these parameters artificially in order to gauge their importance in the calculation of anisotropy. For strong channels with good statistics, this led to an estimate of about $\pm 0.03$ error for $\beta$. In a double coincidence event the mean value of the two angles is used.

2.1. Results

Bond rearrangement is a well known process which is extensively studied in ion-molecule collisions in small molecules. Bond rearrangement requires first a change in the geometry of the molecule, second the formation of new molecular bonds and finally the dissociation of the original molecular bonds. In the studies presented here we focus upon the bond rearrangement processes in the molecular dication that lead to two ionic fragments. We measure the angular distribution of fragments and the kinetic energy released to the fragments.

Acetylene, water and carbonyl sulphide will be presented briefly here. The angular distribution of the fragment pairs reflect the alignment of the molecule as discussed above. If the alignment of the molecule is preserved during the dissociation then we assume that the dissociation is very rapid. Bond rearrangement implies that several steps are involved before the final measurement is made, but we will show that the angular anisotropy can be rather pronounced even in these complex cases.

2.2. Bond rearrangement in core-electron excitation in acetylene

The ground state of the ethyne molecule is linear with $D_{\infty h}$ symmetry, but the $C1s^{-1}\pi^*1$ core-excited state has a bent equilibrium geometry[22]. The spectrum of the core-ionized state contains both stretch vibrational modes and bending modes. The recent study by Kimberg et al. investigated the alignment of bonds in the final dicationic state after excitation to the $C1s^{-1}\pi^*1$ state [23].
The core-excited state decays rapidly via Auger transitions which populate electronic states in the dication, and dissociation to two or more fragments results. By analyzing the momenta of all fragments produced in dissociation we can filter out events connected with isomerization and deformation from the linear geometry. We discuss two-body dissociation of the ethyne dication focusing on the C\(^+\)\(_2\) + H\(^+\)\(_2\) fragmentation channel which is indicative of the bond rearrangement process initiated by the \(\textit{cis}\) bending vibrational mode in the core-excited state. Momentum imaging measurements on the ethyne dication studied after C 1s electron excitation to the \(\pi^*\) valence orbital at 285.7 eV were carried out. A variety of different dissociation channels are measured and a detailed analysis has been carried out earlier [24].

\[\text{Figure 3. (a) A model for the bond rearrangement process in core-excited acetylene is sketched. The core-excited state is the C1s-\(\pi^*\) state, the LUMO of the acetylene molecule. This state is known to have both bending and stretching vibrational modes, and the \(\textit{cis}\) bending mode is proposed as the mechanism for initiating the collapse of the molecule. Note that the original alignment of the molecule is with the linear molecular axis perpendicular to the polarisation direction.}\]

The results are shown in Fig. 3. A model showing the steps leading from the linear acetylene molecule via the core-excited state is presented together with the measured fragment angular distributions. Note that the molecule in the core-excited state is aligned perpendicular to the polarisation vector originally and that despite the fact that the molecular geometry is changed the original alignment is essentially unchanged. The dissociation now takes place with the bond break parallel to the polarisation and the anisotropy is very clear. The sharpness of the anisotropy indicates that the deformation and the subsequent dissociation is very rapid, and that it takes place before the molecule has rotated. The fact that the original alignment is reflected in the anisotropy of this ion pair confirms this.

Calculations of the potential surface indicate that on the basis of energetic considerations the molecule in the core-excited state may rapidly rearrange to a \(\textit{cis}\) configuration within the core-hole lifetime [7]. The dicationic states populated from these new geometries will be preferentially to bent geometries. Palaudoux and Hochlaf identified a dibridged configuration with a \(\textit{cis}\) configuration in the dication which correlates to C\(^+\)\(_2\) (\(a^2\Pi^+\)) + H\(^+\)\(_2\) (\(X^2\Sigma^+_g\)) [5]. They predict an elongation of both the C-C bond and the C-H bonds which is a prerequisite for bond rearrangement. This channel thus competes with other dissociation channels leading to the same \(\text{C}_2 + 2 \text{H}^+\) fragment pair accessible from the same potential-energy surface.
Figure 4. The angular distribution of the fragment pair H$_2^+$ + O$^+$ is shown in the x,y plane. The direction of the polarisation vector is indicated in both plots. (a) The photon energy corresponds to the maximum of the resonant peak for the O 1$s^1$ - 4$a_1^{1+}$ state at 534 eV. The anisotropy parameter for this distribution is $\beta = 1.62 \pm 0.07$. (b) The photon energy corresponds to the maximum of the resonant peak for the O 1$s^1$ - 2$b_2^{1+}$ state at 536 eV. The anisotropy parameter for this distribution is $\beta = -0.67 \pm 0.07$.

Our measurements do not detect a significant signal from this ion pair at any other near-edge resonances but a weak signal is measured at the shape-resonance peak at 320 eV. This is in contrast to the partial ion-yield spectrum measured by Piancastelli, et al. who found the H$_2^+$ species is produced throughout the near-edge excitation region [25]. While our measurement exclusively probes bond rearrangement in the dication species the measurement of Piancastelli probes a broader set of mechanisms including bond rearrangement in the neutral and cation species. In addition secondary bond formation may take place after dissociation.

In conclusion, our experimental angle-resolved fragment distributions of the C$_2^+$ + H$_2^+$ ion pair indicate a rapid geometry change in the core-excited state followed by rapid electronic decay that populates dication states. The fact that this channel is detected only at the C1$s^{-1}1\pi^{+1}$ core-excited state supports the conclusion that the symmetry break due to the cis bending mode drives the bond rearrangement process.

2.3. Core-electron excitation in water

We have studied the fragmentation of molecular dications populated via core-electron excitation to the O 1$s^{-1}4a_1$ and O 1$s^{-1}2b_2$ states in gaseous water molecules from an effusive jet. The main fragmentation channel presented here is the fingerprint of bond-rearrangement, the H$_2^+$ / O$^+$ channel. We have used linearly-polarised synchrotron radiation to excite water molecules, and previous studies by our group have investigated the dipole-induced alignment of the molecule in the excited state and several dissociation channels [27]. The experimental results on the bond rearrangement process are shown in Fig. 4. The plot shows the distribution of the ion pair measured in the imaging spectrometer in the detector plane (x,y). The first panel (a) shows the distribution measured at the O 1$s^{-1}4a_1$ state, and the alignment of the bond-rearrangement dissociation process is striking. From the original molecular alignment with the symmetry axis of the molecule parallel to the electric field polarisation vector the bond angle is closed forming a new bond between hydrogen atoms before the O-H bonds break. The final bond break may well be considered to be a single bond at this point.

This bond rearrangement process in the dication resulting from core-electron excitation of water is detected only at the O 1$s^{-1}4a_1$ and O 1$s^{-1}2b_2$ states in our study and the fact that
this channel appears only at these two resonances implies that nuclear motion originates in the core-excited state with a particular geometry that is favorable for populating dication states with a small bond angle. Ben-Itzhak et al. suggested that the bond rearrangement is the result of a process where the overlap of the initial and final-state wave functions takes place for a favorable geometric situation, and more specifically that a significant barrier must be overcome in order to access this dissociative part of the potential surface[28]. Piancastelli et al. suggested that the bond rearrangement is a consequence of higher vibrational excitation in the molecule. In their study the H$_2^+$ ion yield at the 2b$_2$ peak is slightly displaced to higher energy compared to the photo absorption resonance peak[26].

The present result supports both of these mechanisms if we assume that the necessary internal energy arises in the core-excited state. The preservation of the alignment and the well defined anisotropy constitute evidence that the rearrangement process originates with bending vibrational modes excited at these resonant states, and that the bond rearrangement and dissociation are rapid processes.

2.4. Core-electron excitation in carbonyl sulphide

The carbonyl sulphide molecule is linear in the ground state but the molecular symmetry can be broken by processes such as the Renner-Teller effect. The first unoccupied orbital of $\pi$ character has two degenerate molecular orbitals, one corresponding to a linear geometry and one corresponding to a bent geometry[29]. Population of this state is possible, and will also allow excitation of bending vibrational modes. In the multi coincidence ion spectrum we noted an unexpected ion pair in the double ionisation mass spectrum. In Fig. 5 (a) the ions measured in coincidence with C$^+$ ions are presented and a weak signal at the mass corresponding to OS$^+$ is visible. The OS fragment can only be created if both bonds to the central carbon atom are broken and a bond is formed between the O and S atoms or ions. Given the relatively large mass of all of the atoms making up the carbonyl sulphide molecule identifying this isomerization process is a surprising result. In the OCS molecule, C$^+$ ions have been detected in coincidence with OS$^+$ ions at all photon energies, but at the C1s$\rightarrow$ $\pi^*$ and the two LS-split S2p$\rightarrow$ $\pi^*$ excitations, this pathway has a significantly larger branching ratio, suggesting that nuclear motion is mediated by these core-excitations.

The angular distribution of the C$^+$ + OS$^+$ pair is shown in Fig. 5 (b). The kinetic energy released in the dissociation reaction peaks between 4 and 5 eV, a value which is close to that predicted by Brites, 4 eV[30]. In their calculations of the dication potential surface they predict that for a bond angle greater than about 50° the bond rearrangement channel is open. Our fitting of the anisotropy parameter is displayed in Fig. 5 (b). The best fit is to a value of ($\beta \approx 0.39$) which is far from totally anisotropic but the alignment is roughly parallel to the polarisation vector. This lack of sharply defined anisotropy is suggested to arise from a slow fragmentation process with respect to rotation. This channel gives us important information on nuclear motion in the core-excited state, and we conclude that the photoabsorption process can not be regarded as separate from nuclear motion for this particular case. The bending mode can be excited and the corresponding transition dipole moment is in-plane and perpendicular to the initial C$_{\infty v}$ axis. By selecting the C$^+$/OS$^+$ fragment, we only monitor molecules undergoing a bending motion, with a transition dipole moment aligned with the polarisation axis. The subsequent dissociation retains the memory of this alignment, which is reflected in the intensity distribution of the ejected fragments, parallel to the polarisation vector, $\vec{v}$. We have investigated this hypothesis by looking at the triple-coincidence channel, where we find that the bending motion that causes isomerisation is induced in the C1s$^{-1}\pi^*$ and S2p$^{-1}\pi^*$ state[31].
Figure 5. (a) The coincidence mass spectrum for C 1s-π* excited OCS molecule is shown. All ions which are measured in coincidence with a C\(^+\) ion are plotted on a mass scale and the main fragments, O\(^+\) and S\(^+\) are clearly shown with double peak structures indicating that these bonds were broken parallel to the spectrometer axis, indicating a perpendicular alignment of the linear molecule. A weak OS\(^+\) ion is visible in the mass spectrum and is indicated by the ring. This is the fingerprint of the bond rearrangement process. (b) The angular distribution of the fragment pair OS\(^+\) + C\(^+\). The polarisation direction is vertical as indicated in the polar plot.

2.5. Conclusions
The three examples in this report illustrate how the angular distribution of ionic fragments from molecular dissociation can reflect nuclear dynamics in the weak bond rearrangement channels. Two of these molecules have bond rearrangement that depends essentially on proton migration; and for these two molecules the bond rearrangement is rapid while in the OCS molecule the process is slower, and requires a small bending angle. The origin of the roughly 50° bend is the Renner-Teller effect.

2.6. Acknowledgments
We acknowledge assistance from the MAX-lab staff, in particular to Maxim Tchaplyguine. Funding for this work was granted from the Knut and Alice Wallenberg Foundation, Swedish Research Council (VR) and the Crafoord Foundation. A. S. acknowledges also the Research Council for Natural Sciences and Engineering of the Academy of Finland for financial support. F. A. acknowledges support through the SIDA program administered by the Swedish Research Council.
References

[1] K. Ueda and Eland, J. H. D., J. Phys. B 38, 5839 (2005).
[2] A. I. Chichinin, T. Einfeld, C. Maul, and K-H. Gerice, in Imaging in Molecular Dynamics, edited by B. Whittaker (Cambridge University Press, Cambridge, 2003), pp. 153155.
[3] D. Duflot, J-M. Robbe and J-P. Flament, J. Chem. Phys. 102, 355 (1995).
[4] T. S. Zybina, Y. A Dyakov, S. H. Lin, A. D. Bandrauk and A. M. Mebel, J. Chem. Phys. 123, 134320 (2005).
[5] J. Palaudoux and M. Hochlaf, J. Chem. Phys. 126, 044302 (2007).
[6] R. Thissen, J. Delwiche, J. M. Robbe, D. Duflot, J. P. Flament and J. H. D. Eland, J. Chem. Phys. 99, 6590 (1993).
[7] F. X. Gadea, S. Mathieu, L. S. Cederbaum, J. Mol. Struct (Theochem), 401, 15 (1997).
[8] T. Osipov, C. L. Cocke, M. H. Prior, A. L. Landers, Th. Weber, O. Jagutzki, L. Schmidt, H. Schmidt-Böcking and R. Dörner, Phys. Rev. Lett., 90 233002 (2003).
[9] A. Hishikawa, A. Matsuda, E. J. Takahashi and M. Fushitani, J. Chem. Phys. 122, 151104 (2005).
[10] J. Palaudoux and M. Hochlaf, J. Chem. Phys., 126, 044302 (2007).
[11] R. Thissen, J. Delwiche, J. M. Robbe, D. Duflot, J. P. Flament and J. H. D. Eland, J. Chem. Phys. 99, 6590 (1993).
[12] I. Ben-Itzhak, A. Sayler, M. Leonard, J. Maseberg, D. Hariharamani, E. Wells, M. Smith, J. Xia, P. Wang and K. Carnes, Nucl. Instrum. Methods Phys. Res. B, 233, 284 (2005).
[13] J. H. D. Eland, Chem. Phys., 323, 391 (2006).
[14] K. Tan, C. E. Brion, P. Van der Leew and M. Van der Wiell, Chem. Phys., 29, 299 (1978).
[15] I. Hjelte, M. N. Piancastelli, R. Fink, O. Björnholm, M. Bässler, R. Feifel, A. Giertz, H. Wang, K. Wiesner, and A. Ausmees, Chem. Phys. Lett., 334, 151 (2001).
[16] F. A. Rajgara, A. K. Dharmadhikari, D. Mathur and C. P. Safvan, J. Chem. Phys., 130, 231104 (2009).
[17] A. Hiraya, K. Nobusada, R. Fink, O. Björnholm, M. Bässler, R. Feifel, A. Giertz, H. Wang, K. Wiesner, and A. Ausmees, Chem. Phys. Lett., 334, 151 (2001).
[18] M. Bässler, A. Ausmees, M. Juvantsuu, R. Feifel, J.O. Forsell, P. de Tarso Fonseca, A. Kivimäki, S. Sundin, S. L. Sorensen, N. Ryholm, O. BJörnholm, S. Aksela, and S. Svensson, Nucl. Instrum. and Meth., 469, 382 (1999).
[19] J. Laksman, D Céolin, E. Månssson, S. L. Sorensen, and M. Gisselbrecht, submitted to Rev. Sci. Instrum. (2013).
[20] R. Zare, Mol. Photochem. 4, 1 (1972).
[21] N. Saito, F. Heiser, O. Hemmers, K. Wieliczek, J. Viehhaus, and U. Becker, Phys. Rev. A, 54, 299 (1996).
[22] Y. Ma, F. Sette, G. Meigs, S. Modesti and C. T. Chen, Phys. Scr. 41, 383 (1990).
[23] V. Kimberg, K. Kosugi, and F. Gel’mukhanov, J. Chem. Phys. 130, 114302 (2009).
[24] J. Laksman, D. Ceolin, M. Gisselbrecht, S. E. Canton, and S. L. Sorensen, J. Chem. Phys., 130, 244305 (2009).
[25] M. N. Piancastelli, W. C. Stolte, G. Öhrwall, S.-W. Yu, D. Bull, K. Lantz, A. S. Schlachter and D. W. Lindle, J. Chem. Phys., 117, 8264 (2002).
[26] J. Laksman, E. Månsson, S. L. Sorensen, and M. Gisselbrecht, submitted to Rev. Sci. Instrum. (2013).
[27] J. Laksman, D Céolin, C. Grunewald, A. Sankari, M. Gisselbrecht, D. Ceolin, and SL Sorensen, Phys. Chem. Chem. Phys. 15, 19322 (2013).
[28] I. Ben-Itzhak, A. M. Sayler, M. Leonard, J. W. Maseberg, D. Hariharamani, E. Wells, M. Smith, J. Xia, P. Wang, and K. D. Carnes, Nucl. Instrum and Meth B, 233, 284 (2005).
[29] J. Laksman, D. Ceolin, A. Hempelmann, F. Heiser, O. Gesner, A. Rüdel and U. Becker, Phys. Rev. A 59, 300 (1999).
[30] J. Laksman, D Céolin, M. Gisselbrecht, and S. L. Sorensen, J. Chem. Phys., 133, 144314 (2010).