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Outer-Shell Double Photoionization of CH₄ and CH₂Cl₂ Molecules

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Abstract

In this work the roles of the shake-off and knockout processes in the double photoionization of the CH₂Cl₂ and CH₄ molecules have been studied. The probabilities for both mechanisms accompanying valence-shell photoionization have been estimated as a function of incident photon energy using Samson's (1990) and Thomas's (1994) models, respectively. The experimental results are in qualitative accord with the models.

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1. Introduction

Electron correlation in molecules is currently a significant but difficult study subject due to its small cross sections and its many-body qualities. The ionization of multi-electron targets due to photoabsorption is commonly a weak process in comparison to single photoionization and it is determined completely by electron correlation [R. Whehlitz (2010)]. However, photoionization is the key process to understand electron correlations in molecules. Double ionization probabilities of outer-shell electrons are small, although definite, and are due to shake-off (SO) and the so-called two-step one (TS1), or knock-out, mechanisms, corresponding to sudden and adiabatic processes,

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respectively [T. Schneider et al. (2002), T. Darrah Thomas (1984), P. Lablanquie et al. (2011), J. A. R. Samson (1990), J. A. R. Samson et al. (1992), A.C.F. Santos et al. (2003), T. Pattard et al. (2003)]. In SO, a high-energy transfer occurs between the incident photon and the ejected electron. The photoelectron leaves the target quickly and, consequently; the target electronic cloud feels a sharp change, causing the ejection of a slow electron (SO is described as an overlap between the initial and final target wave functions). In the sudden approximation approach, the SO probability is independent of the photon energy. Although SO is substantially specified in the high-energy region, its significance at intermediate photon energies is still not determined and has been the theme of discussions [T. Pattard et al (2003)].

The TS1 mechanism demands absorption of a low-energy photon by one of the target electrons. It can be regarded as a photoelectric effect accompanied by a single ionization of the leftover ion by the photoelectron. Throughout the process, the photoelectron stays close to the target during a time long enough to knock out the second electron as it leaves. TS1 prevails near the double ionization threshold since the Coulomb potential between the photoelectron and the second ionized electron is maximum in this region. Consequently, the TS1 probability depends strongly on the velocity of the photoelectron. A formal analysis of SO and TS1 in the double photoionization was performed by Schneider and co-workers [T. Schneider et al. (2002)]. They ascertained that both processes are independent from each other and can be obtained separately to find the respective cross sections.

Methane is the most abundant of the minor constituents in the upper atmospheres of the outer planets: Jupiter (0.3%), Saturn (0.4%), Uranus (2%), and Neptune (1.5%). As such, it is the dominant continuous photoabsorber in these atmospheres. Saturn's satellite Titan contains 1.6% methane in its atmosphere, periodically raining liquid methane onto its surface, and it has methane spewing volcanoes and methane lakes near the polar regions. Methane has been detected in meteorites, in comets tails and in young stars in molecular clouds. Traces of methane gas are also present in the Earth's and Mars atmosphere.

The CH_2Cl_2 molecule is a highly symmetrical molecule. It has several important technological applications, it is also routinely employed as a solvent, refrigerant, and aerosol spray propellant, with lasting impact on the ozone layer, even though it is an alternative to the potentially more dangerous HCFC compounds, such as the CHFCl_2 .

In this paper, we present the TS1 and SO probabilities accompanying outer-shell photoionization of the Dichloromethane (DCM) and methane molecules as a function of incident photon energy in order to study the saturation effect of the SO mechanism experimentally and to estimate the relative importance of the adiabatic process.

Experiment

The experimental setup has been described in detail in a previous paper [K. F. Alcantara et al (2011)] and only the significant points for this study are recalled. In brief, experiments were performed at the Toroidal Grating Monochromator TGM beamline of the Brazilian synchrotron light laboratory in Brazil (LNLS). VUV and soft X-ray photons cross an effusive gaseous CH_2Cl_2 (DCM) sample from a hypodermic needle. A neon gas filter was employed to cut down stray light beams and higher-order harmonics. During the measurements, the chamber pressure was kept around 10^{-6} Torr to avoid charge transfer between the recoil ion and the background.

A Wiley and McLaren [W. E. Willey and I. W. McLaren (1955)] time-of-flight (TOF) spectrometer was employed for the charge and mass analysis of the ionic species. The PhotoElectron-PhotoIon-PhotoIon coincidence (PEPIPICO) technique, where at least one of the ejected electrons and two positive ions are detected, was adopted to obtain bidimensional mass spectra. The TOF was projected to possess a maximized collection of ions with energies up to 30 eV.

It is well known that second order photons may influence strongly the photoionization outcomes [R. Whelhlitz (2010)]. Notwithstanding, at higher photon energies of the TGM beam line, the higher-order yield is lessened. However, they are significant at lower energies. By comparing the yield of N_2 with the reported one in the literature [W. C. Stolte et al. (1998)], it can be seen that above 40 eV there is no significant contribution of second order photons. Stray light beams are also a source of error, consisting of scattered photons from the surfaces of the optical elements. Stray photons have a wide wavelength spectrum with significant contributions from low energies (few eV). We have used three diffraction gratings, each one for its specific range of energy. We observed stray light

contributions at the upper energy end of the first grating (~ 90 eV), because the angle of the grating is favorable for scattering photons to the experimental setup. Those contributions were removed and not taken into account in this paper.

The data gathered by the time to digital converter (TDC) is an ordered array of coincidences of ion arrival times related with a removed electron. Due to the dead time limitation of the TDC, no pairs are registered if the second ion arrives within 20 ns of the first one. In addition, due to the limited detection efficiencies, some double coincidence events fall into the single coincidence spectra. With the objective to process the number of double coincidence outcomes that go down into the single coincidence spectra, we have carried out the same routines described previously [K. F. Alcantara et al. (2011)], where the electron and ion detection efficiencies were determined adopting the routines of Simon and co-workers [W. E. Willey and I. W. McLaren (1955)].

Results

The DCM molecule is an alkyl halide and has 42 electrons, where 20 of them are valence electrons distributed according to the following configuration [K. F. Alcantara et al (2011)]: $[3b_1]^2 [7b_2]^2 [9a_1]^2 [2a_2]^2 [6b_2]^2 [8a_1]^2 [2b_1]^2 [7a_1]^2 [5b_2]^2 [6a_1]^2$. However, the ordering of the electronic states differs according to different authors. The first four outer orbitals are essentially non-bonding orbitals of chlorine lone pairs (Cl $3p$ in nature), followed by two C-Cl bonding, two C-H bonding, and the last two are Cl $3s$ in nature.

The photon energy range, from the double ionization threshold up to the Cl 2p edge (~ 200 eV), should be enough to open all fragmentation channels associated with the direct single and double ionization/excitation of valence-shell electrons and unoccupied states of low energy of the neutral or ionized DCM molecule. For those processes, Auger decay is not energetically allowed and the double ionization of the molecule takes place by shake-off (SO) or adiabatic double ionization (TS1).

In the present photon energy range (below the Cl 2p edge), most of the formed doubly-charged DCM ions dissociate quickly into cation fragments by symmetric charge separation ($m^{2+} \rightarrow m_1^+ + m_2^+$), and only a very tiny contribution of dications was observed on the microsecond scale. Thus, in this paper, we shall concentrate in the double photoionization processes that give rise to two singly charged cations. Figure 1 shows the PEPICO projections as a function of the time-of-flight of the fragments of the doubly ionized CH_2Cl_2 molecule. The PEPICO spectra are dominated by the following coincidences: H^+/Cl^+ (25-30 % of all double ionization events), $\text{CH}_2^+ + \text{Cl}^+$ (~ 15 %), CH^+/Cl^+ , C^+/Cl^+ , and H^+/C^+ (~ 10 % each). Due to the limited statistics, only the most intense coincidences will be dealt with here.

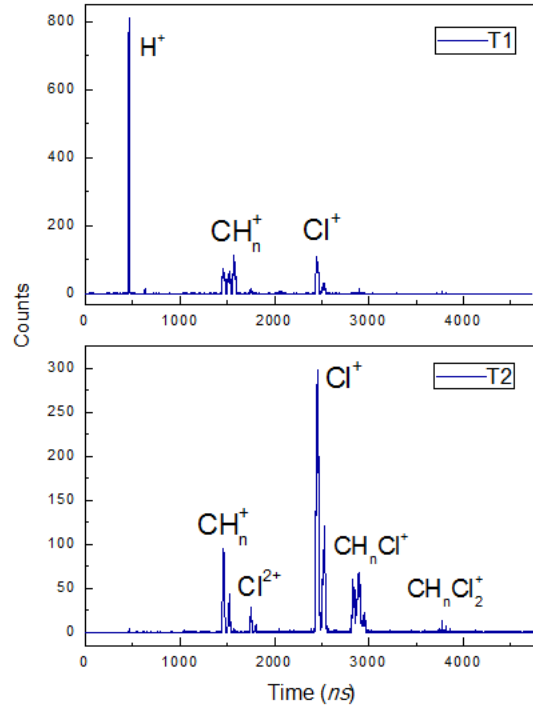


Fig. 1 – Projections of the PEPICO spectrum as a function of the time T1 (time to arrive the first fragment or the first fragment) and T2 (time to arrive the second fragment) of the CH_2Cl_2 molecule after double photoionization at 80 eV.

It is possible to obtain the contribution of the SO mechanism through the shake energy, ΔE , and the energy excess above the threshold, ε . In the case of double ionization of an outer shell, the shake energy is the second ionization potential, and the energy excess is the difference between the energy transferred to the molecule and the ionization potential [T. Darrah Thomas (1984)]. Thomas pointed out that if t_o is the time for the photoelectron to cross the molecular dimension r , SO dominates if $t_o \Delta E / \hbar \ll 1$. The SO probability is given by [T. Darrah Thomas (1984)]

$$P_{SO}(\varepsilon) = P_{SO}(\infty) \exp\left(\frac{-m_e r^2 \Delta E^2}{2\hbar^2 \varepsilon}\right) \quad (1)$$

where $P_{SO}(\infty)$ is the asymptotic SO probability. Equation 1 predicts that the SO process increases steeply above threshold up to a constant value. Thomas' formula has been largely adopted to describe experimental double photoionization data [M. Simon et al. (1991), T. Mukoyama (2009 T. Mukoyama (2010)]. Nevertheless, Eq. 1 fails near threshold, yielding SO probabilities larger than the experimental data. In addition, it neglects the small energy transfer due to the TS1 contributions.

The cross sections for electron impact ionization of a singly charged ion furnish information about the TS1 probabilities. Samson [J. A. R. Samson (1990), J. A. R. Samson et al. (1992)] noted similarities between the double photoionization and the cross sections for single ionization of a singly charged ion by impact of electrons not only for He but also for heavier targets. The ratio of the double-to-total photoionization of a target A is proportional to the single ionization cross section by impact of electrons for the ion A^+ [J. A. R. Samson (1990), J. A. R. Samson et al. (1992)]. This picture is endorsed by experimental data by inspection of double ionization data by photon impact with single ionization by impact of electrons at lower energies. Thus, the TS1 probability for double photoionization

of the target A can be written as

$$P_{TS-1}(h\nu) = \frac{\sigma_{h\nu}^{2+}(h\nu)}{\sigma_{h\nu}^{total}(h\nu)} \cong \frac{\sigma_e^+(h\nu - I_p^+)}{\pi r^2} \quad (2)$$

where the fitting parameter I_p^+ and r are interpreted as the ionization potential and the radius of the ion DCM⁺, respectively. For the chlorine ion, $r = 0.75 \text{ \AA}$ [T. Mukoyama et al. (2010)]. Equation 2 is valid only for the outer valence shell ionization. As SO becomes important, the double photoionization is expected to deviate from the electron impact ionization. The outer shell electrons of the DCM molecule belong to the non-bonding orbitals of chlorine (Cl $3p$ in nature). We have estimated the double ionization potential of the DCM molecule as $I_p^{2+} = 31.6 \text{ eV}$, by adopting the well known empirical rule $I_p^{2+} = 2.8I_p^+$ [W. Lotz (1967)], where $I_p = 11.3 \text{ eV}$ [K. F. Alcantara et al. (2011)]. This estimate is consistent, since it reproduces values in the literature [R.P. Granta et al. (1999)]. Thus, to estimate the ionization potential of the ion CH_2Cl_2^+ , a simple estimate can be done: $I_p^+(\text{DCM})$ is equal to the difference between the double-ionization potential of the target, $I_p^{2+}(A)$, and the single-ionization potential $I_p(A)$, because the ion is already singly charged [R. Whehlitz (2010)]

$$I_p^+(\text{DCM}) = I_p^{2+}(\text{DCM}) - I_p(\text{DCM}) = (31.6 - 11.3) \text{ eV} = 20.3 \text{ eV} \quad (3)$$

The result of Eq. 3 is close to the single ionization potential of Cl^+ (23.8 eV) [R.P. Granta et al. (1999)], as the ejected electrons in the DCM molecule come preferentially from the outer Cl $3p$ orbitals. In the absence of experimental data, the Lotz's formula has been adopted [W. Lotz (1967)] in order to estimate the single ionization of the DCM molecule

$$\sigma(E) = a \frac{\ln\left(\frac{E}{I_p}\right)}{EI_p} \quad (4)$$

where $a = 4.5 \times 10^{-14} \text{ cm}^2 \text{ eV}^2$. Equation 4 is known to give a reasonable measure of direct single ionization of neutral and ionic species by electron impact. The Lotz's formula can be compared with a classical electron-impact scaling law for hydrogenic isoelectronic sequence $\sigma_e(E)I_p^2 = f(E/I_p)$ [W. Lotz (1967)], where $f(E/I_p)$ is a universal function. Thus, the electron impact cross section is proportional to a general curve where the energy is scaled in units of the target ionization potential. Using the scaling parameters from ref. [W. Lotz (1967)], it is possible to reproduce the Lotz's formula within 30%. The electron energy E in the Lotz's formula has been shifted accordingly by using Eq. (3) in order to compare the experimental double-to-total photoionization ratios with the TS1 probabilities.

Figure 2 shows the double-to-total ionization ratio as a function of the photon energy for the DCM molecule. It also compares the experimental data with the SO and TS1 probabilities using Eq. 1 and 2, respectively. By using Thomas' formula in Eq. (1) one obtains $P_{SO}(\infty) = 0.08 \pm 0.1$ and $r = 3.6 \text{ \AA}$, adopting $\Delta E = 11.3 \text{ eV}$ [K. F. Alcantara et al (2011)]. By using $r = 3.6 \text{ \AA}$ in Eq. (2), we can qualitatively describe the double-to-total photoionization ratio at low photon energies, which indicates a consistency between the two models. The shoulder-like structure around 60 eV, approximately equivalent to the average kinetic energy of the valence electrons of the DCM molecule, can be interpreted as due to the contribution of the TS1 process, where the velocity of the photoelectrons matches the velocity of the outermost electrons in the molecule. The lower double-to-total ionization fraction in DCM, in comparison to rare gas atoms [A. C. F. Santos et al. (2005), D. M. P. Holland et al. (1979)], may be attributed to the fewer many-electron correlations in DCM because of its larger volume. It can be seen from Fig. 2 that, besides a pre-edge effect that gradually increases the double ionization cross sections, from the double ionization threshold up to the Cl $2p$ core at about 200 eV, the core electrons of the DCM molecule stay as spectators and do not participate in the photoionization. Around the Cl $2p$ edge, it can be observed that the double-to-total ratio increases steeply as a function of the photon energy. The behavior can be modeled qualitatively by using the

function [F. Von Bush et al. (2004)]

$$\sigma(h\nu) = \sigma(E_\infty) \left[\frac{1}{2} + \frac{1}{\pi} \operatorname{arctg} \left(\frac{h\nu - E_o}{\Gamma/2} \right) \right] \quad (5)$$

where E_o is the ionization potential and Γ is the width of the core hole state.

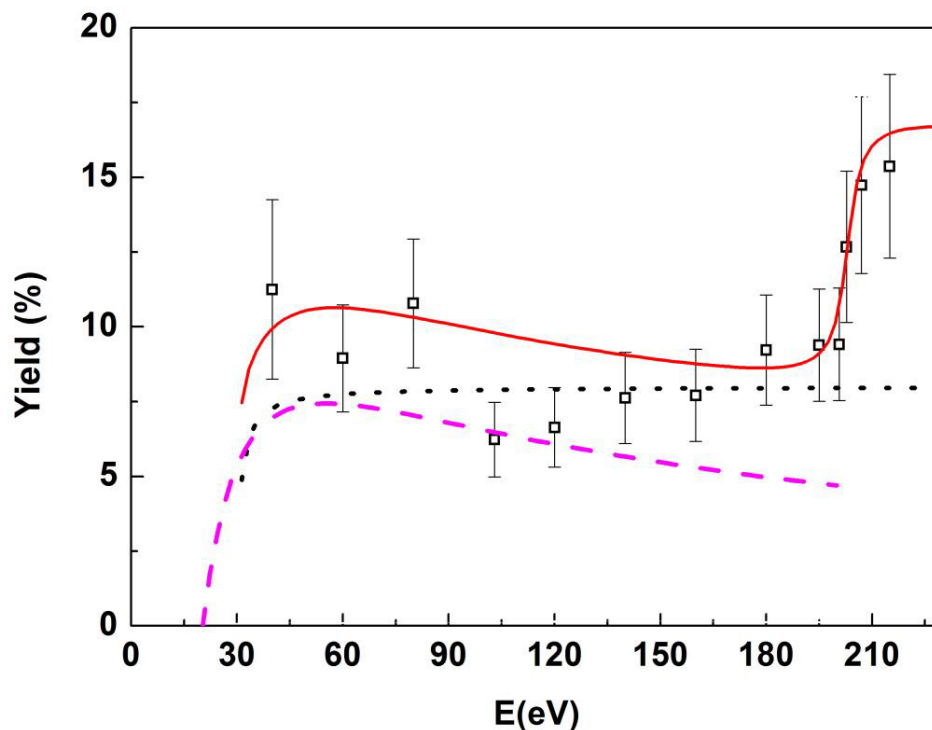


Fig. 2 - Double-to-total photoionization ratio as a function of the photon energy for the DCM molecule. Dashed line: TS1 from Lotz's formula (Eqns. 2 and 4) with $r = 3.6 \text{ \AA}$. Dotted line, Thomas' model for shake-off with $P_{SO}(\infty) = 0.08$ and $r = 3.6 \text{ \AA}$. Full line: SO (Eq. 1) + TS1 (Eqns. 2 and 3) + Eq. (5). The vertical lines indicate the valence and core energy levels of the CH_2Cl_2 molecule.

Figure 3 shows the double-to-total ionization ratio as a function of the photon energy for the CH_4 molecule as well as the corresponding double-to-total photoionization ratio for the isoelectronic Ne target for the sake of comparison. It also compares the experimental data with the SO and TS1 probabilities using Eq. 1 and 2, respectively. By using Thomas' formula in Eq. (1) one obtains $P_{SO}(\infty) = 0.08 \pm 0.1$, adopting $\Delta E = 30.5 \text{ eV}$ [P. E.M. Siegbahn (1982)]. Again, the lower double-to-total ionization fraction in methane, in comparison to Ne [A.C. F. Santos et al. (2005), D. M. P. Holland et al. (1979), G. R. Wright and M. J Van der Wiel (1967)], may be attributed to the weaker many-electron correlations in methane because of its larger volume.

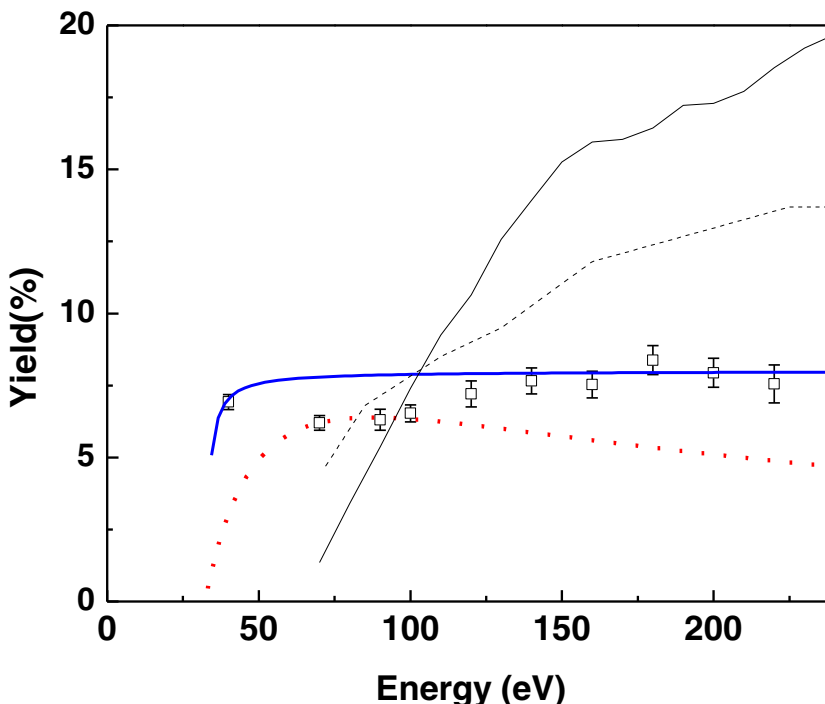


Fig. 3 – Double-to-total photoionization ratio as a function of the photon energy for the Methane molecule. Dashed red line: TS1 from Lotz's formula (Eqns. 2 and 4). Full line, Thomas' model for shake-off with $P_{SO}(\infty) = 0.08 \pm 0.01$. For the sake of comparison, the corresponding double-to-single photoionization of Ne data are also plotted. Solid black line [G. R. Wright and M. J. Van der Wiel (1967)]; dashed black line [D. M. P. Holland et al. (1979)].

Conclusions

We have considered the photon-energy dependence of the double-to-total photoionization ratios for the CH_2Cl_2 and CH_4 molecules from the outer-valence to high photon energies. It was demonstrated that the symmetric fragmentation resulting in two cations plays an important role in the double-photoionization of the CH_2Cl_2 molecule. The SO contribution to the experimental data, for the ion-yield intensity of the double ionization cross section in relation to the total photoionization cross section as a function of the incident photon energy, was fitted to the Thomas' model while the Lotz's formula was used to estimate the TS1 contribution. The models provide good qualitative fits to the experimental data for both molecules. The SO probability at the sudden limit was found to be $PSO(\infty) = 0.08 \pm 0.01$ for CH_2Cl_2 molecule and be $PSO(\infty) = 0.08 \pm 0.01$ for CH_4 molecule.

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