Photodissociation Dynamics of ClCN at Different Wavelengths

Stephan Lutz and Markus Meuwly*[a]

The photodissociation dynamics of small molecules in the gas and condensed phase is an important source of information for better characterizing intermolecular interactions. Herein, classical molecular dynamics simulations with provisions to follow reactive processes between different electronic states are used to probe the wavelength dependence of product state distributions after laser excitation of ClCN. It is found that the maximum of the rotational excitation distribution $P(j)$ of the CN product shifts to lower $j$-values with increasing wavelength and the width of the distribution narrows. Both observations are in accord with earlier experiments and provide improvements over previous theoretical treatments of the process with the same interaction potentials. For the reaction in a water droplet, strong quenching of rotational excitation is found.

1. Introduction

Dissociation reactions play an important role in different fields of chemistry and molecular processes. They are involved in any kind of substitution and elimination reaction in organic chemistry.[1–7] Most rearrangement reactions also involve at least one disruption of a bond.[8–13] Such bond dissociations are mainly of “chemical” nature and are characterized by electron redistribution[14–17] through availability of more favorable bonding partners or through external driving forces such as environmental conditions (solvent or temperature).[18–20] Furthermore, many atmospheric reactions are also of this type. Ozone depletion through the presence of chlorofluorocarbon in the stratosphere is an example for one of these reactions.[21–23] Another dissociation reaction suggested to occur in atmospheric aerosols in the troposphere is the dissociation of H$_2$SO$_4$ into SO$_3$ and H$_2$O.[24–26]

Photodissociation reactions, that is, dissociation reactions induced through the absorption of photons, have played an important role in elucidating the interplay between intermolecular interactions, ground- and excited-state dynamics and energy flow in small molecules.[27,28] In the gas phase, such reactions are typically considered to occur in a two-step fashion. Starting from a ground state $X$ of molecule ABC with a specific internal energy $E_x$, the absorption of a photon with energy $h\nu$ leads to an activated complex ABC* which decays upon energy transfer between electronic and ro-vibrational degrees of freedom to A + BC. In its final state, BC will again assume a wide range of internal states whose population depends on the available energy and the details of the intermolecular dynamics and energy redistribution mechanisms. More recently, such processes have become important in heterogeneous photo-reactions taking place, for example, at interfaces.[29] Biological processes also rely heavily on photoinduced dissociation. For example, the important bond between the heme iron and small gaseous ligands including O$_2$, NO, CO, or CO$_2$ is photolabile. In proteins such as myoglobin (Mb) or hemoglobin (Hb), the ligands can reversibly bind to an iron-containing heme prosthetic group surrounded by the protein. The kinetics for ligand rebinding largely depends on the nature of the protein environment. Flash photolysis was one of the early techniques that were used to obtain information on such processes in myoglobin.[30] To explore CO rebinding, the ligand is dissociated from the heme iron by using a laser pulse which promotes the system from the ground to an electronically excited state ($^1A^\rightarrow^3A$). Subsequently, the rebinding dynamics is studied by following the concentration of CO rebound in time $t$.

From such time-resolved traces details of the interactions between the ligand and the protein environment can be unveiled. However, the atomistic details are usually hidden because recording structural and dynamical information at the same time in experiments is typically not possible. Therefore, computer-assisted approaches have been developed to provide insight at an atomistic level.[31–33]

Computational studies of dissociation processes have a long history. Due to the complexity of the problem, they initially focused on small molecules including H$_2$O, ClCN, ICN, BrCN, and CH$_3$I, and corresponding algorithms usually remained very specific for each molecule and question of interest. Some elaborate techniques for modeling photodissociation reactions are the exact close-coupling method,[34,35] the adiabatic[36] and energy sudden approximations.[37] The most sophisticated ones are based on time-dependent quantum mechanical methods[38,39] whereas simple but in many cases still satisfactory models are based on classical trajectory calculations.[40,41] Here, electronic excitation is understood as a vertical, Franck–Condon-type transition such as illustrated for ClCN $\rightarrow$ Cl + CN.

[a] Dr. S. Lutz, Prof. Dr. M. Meuwly
Department of Chemistry, University of Basel
Klingelbergstrasse 80, 4056 Basel (Switzerland)
E-mail: m.meuwly@unibas.ch
photodissociation, provided that an ensemble. Molecules that interact with the photons can undergo dissociation through interaction with a subsequent photon. The computational procedure used in the following is based on classical mechanics and is straightforward to extend to photodissociation in the condensed phase.

2.1. Molecular Dynamics Simulations

All molecular dynamics (MD) simulations were carried out with the CHARMM program\(^{[47]}\) with provisions to break and form bonds.\(^{[32]}\) The phase space distribution from which dissociation was initiated was generated from an equilibrium simulation on the ground-state PES. This neglects effects due to zero-point energy which, however, are expected to be small due to the heavy atoms involved. Two systems, CICN in gas phase and CICN surrounded by a water droplet with a radius of 7 Å (89 water molecules), were employed. The water sphere was constrained within the 7 Å radius by a primary shell spherical harmonic model.\(^{[46]}\) Each system was heated to 300 K within 20 ps and equilibrated for 150 ps in the NVT ensemble using a leapfrog-Verlet algorithm and a time step of 1 fs. Next, 5000 snapshots separated by 5 ps were extracted. From this point on, the constraints on the water molecules in the solvated systems were removed. Initial phase space distributions at lower temperatures (20, 75 and 150 K) were generated for the gas-phase system from snapshots at 300 K which were cooled down to the desired temperature within 10 to 20 ps and equilibrated for another 10 ps of NVT simulation.

Reactive molecular dynamics\(^{[31,32]}\) was initially developed to follow bond breaking and bond formation in large systems, such as proteins. For the present application, the method was adapted and extended in a number of ways. Most importantly, the incoming photon has a definite energy \(h\nu\) which allows transitions only to take place if it is resonant with the energy difference between the ground (g) and excited (e) state potential. Therefore, excitation is controlled by the condition [Eq. (1)]:

\[
{h\nu} = V_e - V_g = \Delta V
\]

Along a specific trajectory initiated on the electronic ground state, the condition given in Equation (1) is continuously checked and if a specific conformation \(x\) satisfies the criterion [Eq. (2)]:

\[
|{h\nu - \Delta V(x)}| < \delta E
\]

where \(\delta E\) corresponds to an acceptance threshold which should be representative for the laser bandwidth, an excitation is allowed. Then the PES on which the system evolves is changed from the ground state to the excited state where the dynamics continues. The simulation is terminated when the reaction partners have separated sufficiently and a final state analysis is carried out.

In practice, the simulations are carried out as follows: First, an ensemble \((N \approx 10^4)\) of initial structures and velocities is generated on \(V_g\). A time \(t_i\) is chosen which is the time difference between firing the photon and restarting the trajectory; here
induces rotational excitation due to differences in the shapes of the molecule and the influence of a sudden repulsive force and a torque which induces rotational excitation due to differences in the shapes of $V_c$ and $V_e$. As $V_c$ flattens out with increasing distance, the velocities and rotational excitation converge to final values with increasing particle separation. When the system reaches its final state (usually within a few tens of femtoseconds) the MD simulation is stopped and the resulting trajectories are analyzed. Such a procedure will be used to study the photodissociation of ClCN at different wavelengths $\lambda$ (gas phase and solution) and temperatures (gas phase) in the following.

2.2. Interaction Potentials

Singlet ground- and first-excited-state PES were previously computed using the linear-combination-of-Gaussian-type-orbital (LCGTO) $X_0$ method and fitted to two-dimensional functions $V(R, \gamma)$. Here, $R$ is the Cl-to-CN center-of-mass distance and $\gamma$ is the angle between the vectors $\vec{R}$ and $\vec{r}$, where $\vec{r}$ is the CN bond length (see Figure 1). As the detailed parameters for the ground-state surface were not available, a PES was fitted to electronic-structure calculations at the MP2/6-311 + + G(3df,3pd) level and fitted to a parametrization consistent with the standard CHARMN force field [Eq. (3)]:

$$V_g(r_{C\text{C}}, r_{C\text{N}}, \theta) = k_{C\text{C}} \left( \frac{r_{C\text{C}} - r_{C\text{C}e}}{2} \right)^2 + k_{C\text{N}} \left( \frac{r_{C\text{N}} - r_{C\text{Ne}}}{2} \right)^2 + k_{\theta} \left( \theta - \theta_0 \right)^2$$

(3)

Here, $k_{C\text{C}}$, $k_{C\text{N}}$ and $k_{\theta}$ are the harmonic force constants of the Cl–C and C–N stretching and Cl–C–N bending vibrations and $r_{C\text{C}e}$, $r_{C\text{Ne}}$ and $\theta_0$ are the corresponding equilibrium coordinates. The force constants were fitted to experimental ground-state vibrational frequencies [33] and the equilibrium geometries were obtained from ab initio optimization at the MP2/6-311 + + G(3df,3pd) level of theory carried out with the Gaussian 03 suite of programs [33]. The complete set of ground-state force-field parameters are listed in Table 1. For the excited state, the original form [Eq. (4)]:

$$V_e(R, \gamma) = A e^{-\alpha \gamma} e^{-(r_C - r_{C0})^2/2 \beta_C}$$

(4)

was used as was done in other previous work [42,45,46]. Parameters $A$, $\alpha$, $\beta_C$, and $\beta_\gamma$ are also reported in Table 1. For the simulations in a water droplet, the same interaction potentials were used.

2.3. Reactive MD Simulations and Analysis

Adiabatic reactive molecular dynamics [31–33,52] is a surface-crossing algorithm that allows to follow bond-breaking and bond-forming processes in atomistic simulations. The method involves two potential energy surfaces defined by two sets of force-field parameters corresponding to a reactant ($V_c$) and product potential ($V_e$), differing by a number of force field parameters. In view of the present system the simulation is initiated on the bound ground state $V_c$. The possibility for a transition to $V_e$—which plays the role of $V_o$ above—to occur is defined by Equation (2). Because the method was developed for empirical force fields, extensive sampling of the phase space is possible. ARMD simulations were started from each of the 5000 snapshots in the NVE ensemble. Furthermore, the time step was reduced to 0.1 fs for a more accurate leap-frog integration and a higher resolution of the trajectories during dissociation. After $t_0 = 5$ fs in each of the production MD runs the virtual “laser pulse” was initiated. From then on, the energy difference $V_c - V_e$ was compared at every time step until a vertical transition was accepted. The acceptance threshold $\delta E$ [Equation (2)] for a transition was $\pm 5$ kcal mol$^{-1}$, which is typical for the bandwidth of the laser pulse used in the experiments. ARMD simulations were carried out for seven laser wavelengths between $\lambda = 190.6$ nm (150.0 kcal mol$^{-1}$), 6.50 eV) and $\lambda = 213.0$ nm (134.2 kcal mol$^{-1}$, 5.82 eV), namely, at 190.6, 193.0, 196.0, 201.5, 206.0, 208.7, and 213.0 nm at every temperature. Each trajectory was propagated for 500 fs in total. Not every trajectory was reactive. The simulations performed at 20 K in particular show a much decreased number of reactive trajectories. Above $\lambda = 201.5$, no reaction occurred at this temperature (see Table 2).

For every reactive trajectory, the classical analog of the rotational quantum number $j$ was evaluated from the CN rotational angular momentum around its center of mass $L_{CN}^\text{rot}$ [Eq. (5)]:

$$L_{CN}^\text{rot} = \sum_{i=C,N} m_i (r_i - r_{cm}) \times (\vec{r}_i - \vec{r}_{cm})$$

(5)

On average, the gas-phase rotational quantum numbers $j$ evaluated from the present calculations were found to reach their maximum after $\approx 30$ fs of dissociated MD as shown in Figure 2A. In a related calculation, convergence was obtained on a similar time scale. Increasing the wavelength does not appreciably extend the time to converge to the final state but
shows differences in the final \(ji\). In the solvated system (Figure 2B), \(ji\) shows increasingly pronounced periodic fluctuations with increasing excitation wavelength. Figure 2C compares the time series of \(ji\) for the gas-phase simulation for different temperatures. Lowering the temperature has only a weak influence on the time evolution. At 20 K, \(ji\) converges after 30 to 40 fs. Based on this, trajectories were terminated when \(R=11\) Å was reached (corresponding to \(\approx 300\) fs after dissociation) and the final rotational state \(j\) and distributions \(P(j)\) of CN were determined.

3. Results

Photodissociation of CN in ClCN at a wavelength of 193 nm was found to excite the system to a state ClCN* which exerts large bending forces on the triatomic molecule. Rotational spectra measured for dissociating CN(\(X^2\Sigma^+\)) from ClCN show extensive population of rotational states \(J_{\text{CN}}=50\) to 65. Due to the high rotational excitation, photodissociation of ClCN became a paradigm system to study photodissociation dynamics. In the past, preliminary investigations of calculated rotational spectra of ClCN* at 0 and 300 K were carried out while others presented more detailed analysis of the experimentally determined \(P(j)\) at different wavelengths. In the following, results from ARMD simulations as described in the Methods section are compared with the experimental data and with classical and quantum calculations. Figure 3 illustrates the rotational reflection principle from calculations in the gas phase for excitation wavelengths between 190.6 and 208.7 nm. Contrary to the previous study, no transitions were found in the gas phase for excitation at 213.0 nm and are thus not reported. The right-hand side in each panel of Figure 3 reports \(P(j)\) which corresponds to the normalized probability distribution of each set of \(j\) at each excitation wavelength. Two observations can be made by comparing \(P(j)\) between the different panels. First, peak maxima \(j_{\text{max}}\) of \(P(j)\) range from \(j_{\text{max}}=52\) to \(j_{\text{max}}=57\). Previous distribution functions \(P(j)\) computed from classical and quantum mechanical calculations all peak around \(j_{\text{max}}=60\), irrespective of the excitation wavelength. Those results agree well with experiments for excitation wavelengths between 191.5 to 196.0 nm, but at longer wavelengths, the experimental \(P(j)\) clearly peaks at lower angular momenta. In the present simulations, the trend of a decreasing \(j_{\text{max}}\) with increasing \(\lambda\) is qualitatively reproduced. A second characteristic feature of the experimental \(P(j)\), which is captured by the calculations discussed herein, is its continuous narrowing with increasing excitation wavelength.

To more quantitatively discuss the shape and properties of \(P(j)\), the distributions were fitted to Gamma distributions (Eq. (6)):

\[
P(j) = \alpha^{-1} \frac{\exp(-x/\beta)}{\beta^\alpha T(\alpha)}
\]

as shown in Figure 3. Here, \(\alpha\) corresponds to the continuous-shape parameter. \(\beta\) is the scale parameter and \(T(\alpha)=(\alpha-1)!\) is the Gamma function. With increasing excitation wavelength, \(\alpha\) increases from \(\alpha=76\) at 190.6 nm up to \(\alpha=167\) at 208.7 nm, which goes along with a narrowing of the distribution as indicated by the width \(\alpha(P(j))=\sqrt{\alpha^2}\) in Figure 4. In summary, the present simulations find good agreement with the observations from experiment in that with increasing wavelength:

a) \(j_{\text{max}}\) in \(P(j)\) shifts to lower values (up to \(\lambda=201.5\) nm) and
b) \(P(j)\) narrows up to \(\lambda=208.7\) nm. Both observations were not satisfactorily reproduced in previous simulations.

The left-hand panels in Figure 3 report the average rotational quantum number \(<j|l|j>\) as a function of the angle \(\gamma\) of the
parent molecule and the population $W(g)$ from all 5000 simulations. Together with the rotational distribution $P(j)$ shown in the right-hand panels it describes the propensity of $j_{\text{max}}$ to a specific geometrical condition of $\gamma$ on the ground state potential at the time of photodissociation. This corresponds to the rotational-reflection principle successfully introduced in previous studies, where $P(j)$ “reflects” the angular distribution function $j(\gamma)$ at the time of dissociation. A comparison between the different excitation wavelengths in Figure 3 shows that excitations to $V_1$ in gas-phase and at 300 K occur over a range of $\gamma = 0$ to $8^\circ$ for $\lambda \leq 201.5$ nm with a maximum in $W(\gamma)$ at $\gamma \approx 6^\circ$. At $\lambda = 206.0$ nm excitation is only possible for $\gamma > 4^\circ$ and for $\lambda = 208.7$ nm excitation was only possible in a narrow window $6^\circ \leq \gamma \leq 7^\circ$. Thus, the narrowing interval for allowed angles for photodissociation at longer excitation wavelengths is directly related to the observed narrowing of $P(j)$ (Figure 4) mentioned above.

With a statistically significant number of reactive events, other geometrical properties can be analyzed in more detail. Figure 5 reports the distribution of $R$ at the time of excitation.
for every analyzed wavelength at 300 K. Intermolecular distances, $R$, for which excitations were accepted (see Table 2) range from 2.23 to 2.35 Å. The minimum distance at which photodissociation is possible increases for longer wavelengths and reaches 2.34 Å for excitation at 208.7 nm. The narrower $R$-distribution and the shift to larger $R$-values at longer wavelengths is related to the smaller gap $V_g - V_e$ which restricts the configurations that satisfy the criterion for dissociation.

ARMD also allows us to investigate the process in solution. The simulations were carried out in a small water sphere (see Methods section). The right-hand side of Figure 6 shows $j$-distributions $P(j)$ calculated for solvated CICN at different wavelengths. Contrary to the gas-phase simulations, photoexcitation was even found for $\lambda = 213.0$ nm. As one can see from Table 2, the number of dissociative trajectories in solution decreases earlier but more slowly with increasing excitation wavelength compared to the gas phase. A possible reason for the larger number of excited species at longer wavelengths likely comes from stronger deformations that CICN undergoes through the interaction with surrounding water molecules. This becomes evident by comparing $R(j)$ from solution (left-hand side of Figure 6) and gas phase (Figure 3). In solution, even $\gamma > 8.0^\circ$ was sampled, which was not observed in the gas-phase simulations. The maximum of $P(j)$ at excitation wavelengths of 190.6, 193.0 and 196.0 nm is located at $j_{\text{max}} = 10$ which is considerably lower than in the gas phase. Due to the lower rotational excitation, excess energy is redistributed from CICN to the surrounding solvent molecules. This effect seems to be weakened for excitations above 196.0 nm where higher rotationally excited states can be populated. More detailed analysis of the reaction in solution, such as that done for vibrational relaxation of small diatomic molecules,\textsuperscript{[55]} can be envisaged. However, such work should be based on improved interaction potentials for Cl–CN including the effects of the surrounding solvent, which is beyond the scope of the present work.

Finally, the temperature dependence of $P(j)$ in the gas phase at fixed wavelength was considered. For this, calculations at $T = 20$, 75 and 150 K for excitation at 193 nm were carried out. Figure 7 reports the corresponding $P(j)$. The peak maximum of $P(j)$ decreases with temperature and reaches $j_{\text{max}} = 35$ at 20 K. In contrast to all other spectra, the one at 150 K shows a splitting into two favorable rotational quantum states, a major one at $j = 43$ and a less intense one at $j = 54$. For all of these low-temperature rotational distributions, the angular coupling is much less pronounced. The angles of the parent molecules are nearly equally distributed between 0 and $7^\circ$.

4. Discussion and Conclusions

Here, we have discussed reactive MD simulations of the photodissociation of CICN in the gas phase and in a water droplet.
The intermolecular interactions for the excited state have been determined previously whereas the ground-state intermolecular PES was generated from new ab initio electronic-structure calculations. Product state distributions \( P(j) \) are in good agreement with experimental data and a clear improvement over previous simulations is found. In particular, the sensitivity of the maximum \( j_{\text{max}} \) and the shape of \( P(j) \) depending on the excitation wavelength are more realistically captured from the present simulations. It is also possible to follow the reaction in solution and the results (lowering of \( j_{\text{max}} \) and photodissociation yield at longer wavelengths than for the gas-phase reaction) can be rationalized based on the analysis of the trajectories.

The simulation strategies, initially developed for and applied to reactions in the condensed phase,\(^{31-33} \) were found to also provide deeper atomistic insight into gas-phase reactions. To put the current approach into context, it is useful to briefly summarize alternative means to study photodissociation. A detailed account has been given by Schinke.\(^{28} \) In general, classical approaches for electronically excited dissociation consist of three parts: First, choosing initial conditions \( Q_0 \) and \( P_0 \) for the nuclear coordinates and the corresponding momenta and solving the equations of motion on the excited-state PES. Next, each set of initial conditions is weighted according to the distributions of coordinates and momenta in the electronic ground state. Finally, the absorption cross-section is calculated by averaging over phase-space which in practice is done by using Monte Carlo (MC) techniques.

The most pronounced difference between an MC- and an MD-based procedure concerns the weighting of initial conditions in the ground state and the criteria for an electronic transition to occur. In MD simulations, ground-state coordinates and momenta are collected from equilibrium simulations at a specific temperature rather than from stationary and uniform distributions.\(^{44,46} \) Excitations initiated from uniformly distributed ground states result in uniform excited-state distributions [i.e. \( W(j) \)]. Molecules for which such an approach has been taken in the past include \( \text{ClCN,}^{45} \) \( \text{CINO,}^{56} \) \( \text{FNO,}^{53} \) \( \text{H}_2\text{O}_2^{57} \) and \( \text{CF}_3\text{I}^{58} \). In the current approach, the geometrical distribution \( W(j) \) is in most cases non-symmetrical and the distributions \( P(j) \) are in better agreement with the experimentally determined ones, which suggests that the approach pursued here may be preferable. Furthermore, an excitation to \( V_e \) is only accepted if the excitation energy corresponds to the difference between the ground- and excited-state PES. In the MC approaches, the absorption cross-section is used as the criterion whether an electronic transition is accepted or not.

As already pointed out before, the current classical MD approach correctly describes the experimentally observed rotational quantum-number distribution for the photodissociation of \( \text{ClCN} \) in the range of 190.6 to 208.7 nm. Although previous

![Figure 7. Rotational excitation of CN at 193.0 nm for different temperatures. Left: \( W(j) \) and \( \langle j \rangle \) in the range of \( \gamma \) over all trajectories with an observed transition. Right: \( P(j) \) over all successfully dissociated trajectories. Dotted lines (---): fitted probability density of the Gamma distribution.](image-url)
such extensions could also be envisaged for these simulations focused on the dissociation dynamics at surfaces has also been studied using MD-based approaches. Table 2).

Figure 8. Population distribution of the time of dissociation after firing the "laser pulse" over all 5000 trajectories for different excitation wavelengths. Black signals: gas-phase photodissociation at 300 K at the respective wavelengths. The gray traces represent the distributions for photodissociation in solution at 300 K (l = 193 nm), 75 K (l = 201.5 nm), and 20 K (l = 206.0 nm), respectively.

attempts found agreement at shorter wavelengths, the fact that \( \lambda_{\text{max}} \) was essentially insensitive to the excitation wavelength led to the suggestion that other electronically excited states may be involved in the dissociation process. The present results suggest that this is not necessary. Rather, it is found that for excitations at longer wavelengths, a sufficiently strongly bent (\( \gamma \approx 7 \)) CI CN ground-state configuration is populated. Another indication for the decreasing reaction probability with increasing wavelength comes from the cross-section of the CI CN absorption spectrum which decreases rapidly beyond 210 nm. This is reflected in the reaction times at each wavelength which are summarized in Figure 8. The reaction-probability distribution extends to longer times as the wavelength decreases (black). Colored distributions evaluated from simulations at lower temperatures show delayed photodissociation at their longest wavelength allowed for an excitation (see Table 2).

More recently, photodissociation of ICN in solution and at surfaces has also been studied using MD-based approaches. These simulations focused on the dissociation dynamics at fixed wavelength and included nonadiabatic effects in the excited states. Such extensions could also be envisaged for the current approach, as explained earlier. However, the present work is primarily concerned with a detailed comparison to experimental data and the approach has shown to be able to capture atomistic details of the processes involved. Together with the recent work on ICN, it is concluded that classical MD approaches provide very valuable information for statistically meaningful analysis of photodissociation processes in the gas and condensed phase.

Keywords: computational chemistry · electronic states · intermolecular interactions · molecular dynamics · photochemistry


Photodissociation Dynamics of ClCN


Received: July 25, 2011
Published online on November 9, 2011