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Collision induced dissociation of protonated urea with N_2: Effects of rotational energy on reactivity and energy transfer via chemical dynamics simulations

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ABSTRACT

In the present work we have investigated the gas phase reactivity of protonated urea after collision with the diatomic inert gas N_2, by studying the energy transfer and fragmentation induced by collisions. We first developed an analytical pair potential to describe the interaction between the projectile and the ion, and then performed QM/MM direct chemical dynamics simulations of the collision between the projectile and protonated urea in its two most stable isomers. In particular, the effect of the diatomic projectile, and the role of its initial rotational state, were compared with the fragmentation and energy transfer obtained previously (*J. Phys. Chem. A* 2009, *113*, 13853) for the monoatomic projectile Ar. The diatomic projectile was found to be less efficient in energy transfer compared to the monoatomic projectile. In addition, rotational activation of $UreaH^+$ is dependent on the initial rotational quantum number of N_2. Finally, we investigated the $UreaH^+$ gas phase reactivity as a function of its rovibrational activation by means of chemical dynamics simulations where the initial structure for the simulations is the transition state (TS) that the system can reach after collisional activation of the most stable isomer. The simulation time-length is not able to directly access this TS from the most stable isomer since its lifetime is notably longer, of about two order of magnitude in time.

1. Introduction

Collision-induced dissociation (CID) is an important experimental method to study structure and reactivity of a variety of molecular systems, including small molecules [1–3], clusters [4–7], and organic [8–10] and biological molecules [11–15]. In CID, an ion is energised by collisions with a noble gas atom or unreactive molecule such as N_2. In the limit of low energy collisions, electronic excitation is unimportant and the collisions transfer a fraction of the translational energy to vibrational/rotational energy of the molecular ion so that it can eventually dissociate. It is possible to monitor the residual parent and product ions after CID.

Recently, we studied CID of protonated urea by coupling chemical dynamics simulations, RRKM analysis and ESI-MS/MS experiments. In particular we found that, after energy transfer to $UreaH^+$, fragmentation to high energy products occurred, resulting from either non-RRKM effects and/or dynamics driven by the high rotational energy of $UreaH^+$ [16]. In this first study we investigated collisions with Ar, for which an analytic interaction potential was previously developed by Meroueh and Hase [17]. We employed a QM/MM method for the simulations, where the projectile–ion interaction was represented by the above analytic pair potential (MM), while the ion was treated at the MP2 level (QM) in order to allow the system to dissociate.

In many MS/MS experiments N_2 is used as inert collision gas, mainly because of the lower cost compared to noble gases. This gas has a mass higher than Ne and smaller than Ar, but it is often assumed to behave similarly. A detailed study on the effect of the projectile on CID, limited to noble gases, was performed by Anderson and co-workers [18], who demonstrated that Ne, Ar and Kr behave similarly and only Xe leads to a different CID efficiency. N_2, while in the same mass range of "light" noble gases, has internal degrees of freedom and its rotational energy may play a role in energy transfer.

Chemical dynamics simulations [19] can model CID processes by calculating an ensemble of trajectories for which the projectile ion and the inert gas collide with a given relative translational energy and all possible relative collision orientations present in CID

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experiments are sampled [20]. In the case of a diatomic projectile such as N_2, its initial rotational state must also be chosen according to the Boltzmann distribution. At room temperature its vibration is in the ground state. This simulation method, which requires hundreds or thousands of trajectories for statistical relevance, can be done by using an analytic [21] potential energy function or by direct dynamics [22]. For some special cases it is possible to use an analytic function which includes unimolecular decomposition paths for the ion [21], but more common is to use a molecular mechanical (MM) potential for the ion, which does not describe unimolecular decomposition. The latter yields the efficiency of translation-to-vibration (T → V) and translation-to-rotation (T → R) energy transfer in CID [23]. With direct dynamics a quantum mechanical (QM) model is used for the ion and decompositions, which occur during the simulation time-length [22], can be studied. *Ab initio* direct dynamics for CID become very computationally expensive as the size of the ion grows and, thus, it can be useful to treat only the ion by QM and use MM potentials for interactions with its collision partner [23].

An interaction potential of the same (or similar) form as that used previously for Ar/UreaH$^+$ was not available for N_2/UreaH$^+$ and, thus, was first derived in the present study. With this potential we studied energy transfer and reactivity, finding that the rotational energy of a projectile plays an important role. Only one isomer of protonated urea is able to react within the simulation time-length; i.e., there is not sufficient time for the more stable isomer to reach the isomerisation transition state and then eventually react. From energy transfer obtained from the simulations for the more stable isomer, we initiated trajectories from this transition state with the appropriate rotational and vibrational energies. Rotational energy was found to be crucial in determining the reactivity.

2. Computational details

2.1. Potential energy function

The general analytic potential energy function used for the N_2 + UreaH$^+$ system is represented by

$$V = V_{\mathrm{UreaH^+}} + V_{N_2} + V_{N_2/\mathrm{UreaH^+}} \tag{1}$$

where $V_{\mathrm{UreaH^+}}$ is the UreaH$^+$ intramolecular potential represented by MP2/6-31G* *ab initio* calculations (as in Ref. [16]), V_{N_2} is the N_2 intramolecular potential and $V_{N_2/\mathrm{UreaH^+}}$ is the intermolecular potential between the projectile (N_2) and the ion (UreaH$^+$). For the latter two terms we employed analytical pair potentials, whose parameters were obtained from *ab initio* calculations as detailed in the following.

The N_2 intramolecular stretching potential is harmonic, where the equilibrium distance (1.12 Å) and vibrational frequency (2176 cm^{-1}) were obtained from MP2/6-311++G** calculations. The N_2/UreaH$^+$ interaction potential is a sum of two-body terms of the form:

$$V_{N-i} = ae^{-br_{N-i}} - \frac{c}{r_{N-i}^9} \tag{2}$$

where r_{N-i} is the distance between each nitrogen atom of N_2 and each atom, *i*, of UreaH$^+$. This interaction potential expression is the same as the one used and parametrized by Meroueh and Hase for Ar-Peptide CID and recently used by us in QM/MM direct chemical dynamics simulations of Ar-UreaH$^+$ and Ar-[Ca(Urea)]$^{2+}$ [16,24]. Atom–atom parameters were obtained by fitting interaction energy curves obtained from QCISD(T)/6-31++G** calculations with BSSE corrections by employing the counterpoise method [25,26], i.e., the same level of theory as employed in Ref. [17].

To obtain the two-body parameters in Eq. (2), we divided UreaH$^+$ into building blocks, similarly to what was done to obtain parameters for Ar CID simulations of protonated polyglycines [17], where the NH_3, NH_4^+, CH_4 and HCO_2H building blocks were used. The molecules NH_3, NH_4^+, and formic acid were used as the building blocks for UreaH$^+$. For N_2 interacting with each of these molecules, different orientations of both N_2 and the molecules were considered.

Table 1
Intermolecular potential parameters.[a]

Potential	*a*	*B*	*C*
N_2/NH_3 (N_2N)	60,253.8	5.56	0.76
N_2/NH_3 (N_2H)	968.1	1.83	0.15
N_2/NH_4^+ (N_2N)	42,545.1	4.81	1.10
N_2/NH_4^+ (N_2H)	5040.2	3.70	0.02
N_2/HCO_2H (N_2OH)[b]	20,393.7	4.02	3.16
N_2/HCO_2H (N_2HO)	6263.5	4.46	0.17
N_2/HCO_2H (N_2CO)	1344.4	1.41	45.89
N_2/HCO_2H (N_2OC)	19,520.2	4.07	3.27
N_2/HCO_2H (N_2HC)	10,268.5	5.38	0.00

[a] Parameters for Eq. (2) with *a*, *b*, and *c* in units of kcal/mol, Å^{-1}, and kcal Å^9/mol, respectively.

[b] Two-body potential between N_2 and an oxygen atom of the OH group of a carboxylic acid group.

The potentials between N_2 and the N and H atoms of an amine group were determined from N_2/NH_3 *ab initio* calculations, which are shown in Fig. 1. The potential curves are for N_2 interacting with NH_3 front-side and back-side, along the C_{3V} axis, and interacting on the side, with different rotational orientations of N_2, as shown in the same Fig. 1. The interaction between N_2 and the atoms of the protonated amine end group was modelled by interactions of the N_2 and the ammonium molecule. As for the above N_2/NH_3 *ab initio* calculations, N_2/NH_4^+ interactions were calculated for both front-side and back-side C_{3V} interactions, with different N_2 rotational orientations. The *ab initio* and fitted curves are plotted in Fig. 2. The two-body interaction potentials between N_2 and the atoms of a carboxylic group were determined from four sets of *ab initio* calculations for the N_2/formic acid system. Intermolecular potentials were calculated for interactions along the O–H···N_2, C=O···N_2, and N_2···C=O axes and for N_2 interacting with the O atom of OH along an N_2···O axis parallel to the C=O bond (see Fig. 3). Also in this case different N_2 rotational orientations were considered. The potential energy curves for these calculations are given in Fig. 3.

The parameters of Eq. (2) were obtained by simultaneously fitting all the potential energy curves for each system studied. The resulting fits are plotted in Figs. 1–3, and it is seen that there is globally good agreement between the *ab initio* and fitted curves. The potential parameters derived for the two-body potentials are listed in Table 1.

2.2. Collision induced simulations

Two Urea-H$^+$ structures were considered for the direct dynamics simulations: one protonated on oxygen (OPr) and one on nitrogen (NPr), with their geometries optimized at the MP2/6-31G* level of theory (see Fig. 4). As discussed in our previous work [16], the potential energy minimum of NPr, calculated with MP2 using the 6-31G* and aug-cc-pVTZ basis sets, is 9.7 and 13.8 kcal/mol higher in energy, respectively, than that of OPr, corresponding to 9.0 and 13.4 kcal/mol free energy differences, respectively. Thus, for thermal equilibrium conditions there is negligible population of the NPr isomer. However, ESI experiments are likely to be non-equilibrium for small systems as reported by several studies [27–30]. Consequently, there may be a substantial population of NPr. Thus, we considered both isomers, OPr and NPr (as previously done for Ar collisions [16]) for the work presented here, which allow us to compare with the results obtained for the monoatomic projectile Ar.

Initial conditions for each UreaH$^+$ isomer were chosen by adding a quasi-classical 300 K Boltzmann distribution of