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Theoretical investigation of fragmentation effects in the energy deposition of swift ions in formaldehyde

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Abstract. We report the beginnings of a study of the impact of swift alpha particles on the smallest of the protobiological molecules: formaldehyde. We report the kinetic energy release for C, O, and H ions for projectile energies of 1.5, 3.0 and 5.0 keV.

1. Introduction
As experimental methods for the measurement of the properties of ion molecule collisions become more sophisticated, the variety and properties of targets investigated increases. One aspect of this is that larger molecular targets and the effects of their orientation with respect to the beam direction can now be studied. Concomitant with experimental study, theoretical studies have developed, which focus on molecular target fragmentation on collision, and the effect on various collision cross sections.

This becomes of interest on several grounds. A significant step towards the understanding of the origin of prebiotic molecules in interstellar space was made when, on the basis of spectroscopic evidence, Kuan et al. [1] discovered glycine in the interstellar medium. Presumably, this simplest of amino acids is the result of reactive collisions among smaller atoms, molecules, ions, and radicals, in both ground and excited states, many of which are formed as fragmentation products during collisions. It is this rich, but dilute, soup that leads to the proto-biology that is of interest.

A question that one might then ask concerns the origin of many of the molecular ions and radicals that contribute to the interstellar protobiology, and how these objects interact with the interstellar radiation field.

Perhaps a more mundane problem has to do with radiation damage and tumor treatment. When attempting to understand the treatment of a tumor with radiation, it is imperative to know specifically what particles, radicals, ions and fragments, result from the collision.

The various reactions of ions with molecules have several features in common, one of which is the problem of kinetic energy release. When ion induced molecular fragmentation occurs, some of the
excess internal energy of the molecule is released as kinetic energy of the fragments [2]. The Kinetic Energy Release (KER) associated with a reaction gives much information about the reaction itself, and some indications concerning the possible subsequent reactions of the fragmentation products.

As a preliminary incursion in this vast field of ion biomolecule reactions, we report here results of a work in progress involving the KER for the smallest of the prebiotic molecules, CH$_2$O (formaldehyde) undergoing collisions with alpha particles, which we chose as our projectile for the study of fragmentation. Thus, we study the fragmentation patterns for $^3$He$_2^+$ + CH$_2$O at laboratory frame collision energies ranging from 50 eV/amu to 250 keV/amu. [We use $^3$He$_2^+$ rather than the more common $^4$He$_2^+$ as the projectile in anticipation of experimental verification of these predictions: D$^+$ and H$_2^+$ both have the same charge to mass ratio as $^4$He$_2^+$, and thus can interfere with detection.]

2. Methodology
In order to study the fragmentation of formaldehyde by swift alphas, we need to calculate fragmentation probabilities and cross sections. These are the measurable quantities with which theory should be compared.

To calculate a cross section for collisional processes from calculated trajectories, as we do, we adopt the following scheme: If we wish to calculate the cross section for a process leading to a set of products labeled $i$, and if we know the probability, $P_i$, for obtaining those products at projectile energy $E$, then the cross section for the process, $\sigma_E$, is obtained by integrating over impact parameters:

$$\sigma_E = 2\pi \int P_i(b,E) b \, db.$$  \hspace{1cm} (1)

We investigate these processes using a theoretical scheme known as Electron Nuclear Dynamics (END) [3], which is time dependent, direct, and non-adiabatic. As no potential surfaces are required in this approach, the instantaneous Coulomb forces among the participating electrons and nuclei steer the dynamics of the process. The coupling among all electrons and nuclei is explicit. The major advantage of this method is that all possible product channels are open and are considered together, and all at the same level of approximation, thus increasing the reliability of prediction of product distributions. No pre-selection of trajectories is made, and the collision trajectories are determined by the quantum mechanics of the collision only. The scheme conserves total energy, total momentum, and angular momentum. The END scheme has been implemented in the ENDyne code [4], which has been used to obtain the results presented here. We first present an outline of the END method [3-5] and then proceed to present our calculational procedure and discuss our results.

3. Theoretical Structure
Our theoretical approach for analysis of energy deposition by swift $^3$H$_2^+$ ions on formaldehyde is based on the application of the Time-Dependent Variational Principle to the Schrödinger equation, where the wave function is described in a coherent state representation. This is the basis of Electron-Nuclear Dynamics (END). As the details of the END method have been reported elsewhere [3-5], we give only a brief summary of the fundamental features of the theory.

The END theory [3,5] is based on a system wave function

$$\psi(t) = |R(t), P(t)\rangle |z(t), R(t), P(t)\rangle$$  \hspace{1cm} (2)
characterized by a set of time-dependent parameters and a choice of basis set. The first factor on the right hand side of Eq. 2 corresponds to the nuclear wave function

$$R(t), P(t) = \prod_k \exp \left[ -\left( \frac{X_k - R_k}{w} \right)^2 + iP_k \cdot (X_k - R_k) \right]$$

for distinguishable nuclei $X_k = (X_{1k}, X_{2k}, X_{3k})$. Here, $R_k = (R_{1k}, R_{2k}, R_{3k})$ and $P_k = (P_{1k}, P_{2k}, P_{3k})$ are the time dependent average nuclear positions and momenta of nucleus $k$, respectively. The traveling Gaussian wave packets which represent the nuclei have a width, $w$, which, in this application, will be set to zero, implying that the nuclei move as classical particles.

The second factor in the system wave function (Eq. 2) represents the $N$-electron wave function for the combined system of projectile and target:

$$\left| z(t) \right| = \det \left( \chi_i (x_j) \right),$$

where the complex, non-orthogonal, spin orbitals are expressed as

$$\chi_i = u_i + \sum_{j=N+1}^{K} u_j z_{ji} \quad i = 1, 2, \ldots, N.$$  

The atomic spin orbitals $\{u_j\}_{j=1}^{K}$ are written as a linear combination of traveling Gaussian basis functions having the form:

$$\left( x - R_{1k} \right) \left( y - R_{2k} \right)^m \left( z - R_{3k} \right)^n \exp \left[ -\alpha \left( x - R_k \right)^2 - \frac{i}{\hbar} P_k \left( x - R_k \right) \right].$$

The spin orbitals are centered on the nuclei, which have average position $R_k$ and momentum $P_k$.

Equations 4 and 5 describe a so-called Thouless determinant [6], which contains the time dependence in the Thouless coefficients $z_{ji}(t)$. In order to obtain the equations of motion for the system, one applies the time-dependent variational principle to the action obtained from the quantum mechanical Lagrangian of the system

$$L = \left\{ \psi \mid i\hbar \frac{\partial}{\partial t} - H \mid \psi \right\} / \left\langle \psi \mid \psi \right\rangle$$

where $H$ is the system Hamiltonian. From the Euler-Lagrange equations

$$\frac{d}{dt} \frac{dL}{dq} = \frac{\partial L}{\partial q}$$

one obtains the dynamical variables of the system $\{q\}$. In this theory, the $\{q\}$ consist of the complex Thouless coefficients, $z_{ph}$ and $z_{ph}'$, and the average nuclear positions and momenta, $R_{jk}$ and $P_{jk}$.

Again, we note that the formulation used here is in the limit of $w \to 0$ in Eq. 3, namely that the nuclei move as classical particles.

In matrix form, the equations of motion can be written as
Here, the dynamic metric contains the coupling elements:

\[
\begin{bmatrix}
  iC & 0 & iC_R & iC_P \\
  0 & -iC^* & -iC_R^* & -iC_P^* \\
  iC_R^* & -iC_R^T & C_{RR} & -I + C_{RP} \\
  iC_P^* & -iC_P^T & I + C_{PR} & C_{PP}
\end{bmatrix}
\begin{bmatrix}
  z \\
  z^* \\
  \partial E / \partial z \\
  \partial E / \partial z^* \\
  \partial E / \partial R \\
  \partial E / \partial P
\end{bmatrix} = 0.
\]

(9)

Here, the metric contains the coupling elements:

\[
(C_{XY})_{jk,kl} = -2 \text{Im} \frac{\partial^2 \ln S}{\partial X_k \partial Y_l}
\]

(10)

\[
(C_{ab})_{ph} = (C_{ah})_{ph,k} = \frac{\partial^2 \ln S}{\partial z_{ph} \partial X_k}
\]

(11)

\[
C_{ph,qg} = \frac{\partial^2 \ln S}{\partial z_{ph} \partial z_{qg}}
\]

(12)

and

\[
S = \langle z, R', P' | z, R, P \rangle
\]

(13)

is the overlap matrix.

The total energy of the system is given by:

\[
E = \sum_k \frac{P_k^2}{2M_k} + \frac{\langle z, R | H_e | R, z \rangle}{\langle z, R | R, z \rangle}.
\]

(14)

where \(H_e\) is the electronic Hamiltonian of the compound system, and contains the nuclear repulsion energy.

The usual adiabatic coupling terms, \(C_{RR}\), and the non-adiabatic coupling terms, \(C_R\), are evident in Eq. 9. Integration of the system of equations shown in Eq. 9 yields the trajectories of the classical nuclei and their associated electrons [3,5]. It is these trajectories that we report here.

4. Calculational Details

The computation of the collision requires the specification of initial conditions of the system under consideration. The formaldehyde molecule, with \(C_{2v}\) symmetry, is placed in a laboratory fixed coordinate system. A schematic of a \(C_{2v}\) symmetry object is shown in Fig. 1.
FIGURE 1. Orientation of a Schematic C$_{2v}$ Object in a Laboratory Fixed Reference Frame.

The projectile velocity initially is set parallel to the laboratory $z$-axis and directed towards the stationary target with an impact parameter, $b$ in the $xz$-plane. The initial distance of the projectile from the target is set at 20.0 a.u. in the $z$-axis. The range of impact parameters is divided in three regions: from 0.0 a.u. to 2.0 a.u. in steps of 0.1 a.u., from 2.0 a.u. to 5.0 in steps of 0.2 a.u., and from 5.0 a.u. to 15.0 a.u. in steps of 1.0 a.u. for each target orientation, leading to 46 trajectories (impact parameters) per target-orientation/projectile velocity [7]. As we are dealing with an atomic projectile, we need to consider only the orientation of the target. In order to obtain orientational averaged properties, we must perform a target rotation over the Euler angles with respect to the incoming beam. The target is set at the origin of a laboratory coordinate system, with its orientation described by a set of Euler angles [7]. A coarse grid of initial orientations is obtained for increments of 90° in all the three angles with a minimum number of ten independent target orientations for a molecule of $C_{2v}$ symmetry, as is the case here. These orientations are listed in Table 1.

| Orientation | $\alpha$ | $\beta$ | $\gamma$ |
|-------------|---------|---------|---------|
| I1          | 0       | 0       | 0       |
| I2          | 0       | 0       | $\pi$/2 |
| IIa1        | 0       | $\pi$/2| 0       |
| IIa2        | $\pi$/2| $\pi$/2| 0       |
| IIa3        | 3$\pi$/2|$\pi$/2 | 0       |
| IIb1        | 0       | $\pi$/2|$\pi$/2 |
| IIb2        | $\pi$/2| $\pi$/2|$\pi$/2 |
| IIb3        | 3$\pi$/2|$\pi$/2 |$\pi$/2 |
| III1        | 0       | $\pi$  | 0       |
| III2        | 0       | $\pi$  | $\pi$/2|

Thus, we calculate a total of 460 projectile trajectories per velocity. An adaptive time step of initial value $ca. \ 10^{-3}$ a.u. (1 a.u. = 2.6 x $10^{-17}$ sec.) was used. The dynamics is stopped when the projectile is 20.0 a.u. past the target or when no change in the projectile velocity, or electron transfer is observed.
We note that the $C_{2v}$ symmetry designation is for the target molecule in its initial state only, and this symmetry is not maintained during the collision. After the trajectories are calculated and the appropriate cross sections determined, the quantities are orientationally averaged to correspond to a dilute gas target.

The basis sets used to describe the initial ground state of formaldehyde ($\tilde{X}^1A_e$) at the SCF level of theory were those of Dunning [8]. For the hydrogen atom we use a VDZP basis set consisting of \([4s1p/2s1p]\) primitives. For the oxygen atom we use a SV basis set consisting of \([10s5p/3s2p]\) primitives and finally, for the carbon atom, we use a basis set from Schafer \[8\] consisting of \([7s2p/4s2p]\) primitives. Thus, in total we have 38 contracted Gaussian functions to describe a molecular orbital, providing a good description of the electronic state of the system at the projectile energies considered in this work.

5. Results and Discussion

As a step towards an initial understanding of the fragmentation process, we consider the kinetic energy release for fragmentation of formaldehyde when colliding with swift alphas. The direction and energy of the fragmentation products are observables that are directly related to the fragmentation process, and form the basis of inferences concerning the collision process.

In Figures 2 – 4, we present plots of the KER vs. the angle of the ejected atoms/ions with respect to the incoming beam for the ejected C$q^+$ (Fig.2), O$q^+$ (Fig.3), and H$q^+$ ions (Fig.4). The plots are presented as two dimensional density plots for 1.5, 3.0 and 5.0 keV/amu $^3$He$^{2+}$ projectiles colliding with formaldehyde, and the results have been orientationally averaged. We do not report cross sections for polyatomic fragments here, as they cannot be emitted with high kinetic energies. The KER is given in eV, and the color indicates the classical cross section (Eq. 1) in units of $10^{-16}$ cm$^2$ for ejection of an atom or ion (O, C, or H) at a given kinetic energy and atom. The results are for orientationally averaged targets so that they might eventually be compared to experiments.

In these figures, a horizontal cut through the graph yields the variation of cross section at fixed KER as a function of the angle of the ejected fragments with respect to the incoming beam direction, while a vertical cut yields the variation of cross section as a function of KER for fixed ejection angle. It should be noted that there is no differentiation among channels for ions which differ only in charge state. Rather, the cross sections take into account all ions that are produced with a particular KER and ejection angle.

Several common features can be seen in the nine plots presented:

- In all cases, the greatest cross sections come from collisions leading to ions with KER $\leq$ 10 eV.
- In general, the high cross sections are found for ejection angles clustered around 0°, 90°, and 180°.
- The highest KER occurs, in all cases, for zero or very small scattering angle.
- At a given projectile energy, the fastest fragments are protons, which are emitted almost isotropically with respect to the ejection angle.
- Since DNA or protein lesions can be caused by particles with energies of 10 eV or less [9], fragments of the sort reported here could cause DNA damage.

Although no experiments are available for comparison, there are possible connections to be made. We have not calculated time resolved trajectories. However, were we to do so, we could track the trajectories individually and calculate coincidence data. This could be used in conjunction with mass spectrometer data to study each fragmentation channel separately. As we can orient our target molecule at will, it is possible to do directional studies as well.
FIGURE 2. Kinetic energy release vs. fragment direction for C\(^{q+}\) fragments, q = 0-6, at projectile energies of 1.5, 3.0, and 5.0 keV/amu for \(^3\)He\(^{2+}\) + CH\(_2\)O.
**FIGURE 3.** Kinetic energy release vs. fragment direction for O$q^+$ fragments, $q = 0-8$, at projectile energies of 1.5, 3.0, and 5.0 keV/amu for $^3$He$^{2+} + \text{CH}_2\text{O}$.
FIGURE 4. Kinetic energy release vs. fragment direction for $H^{q}$ fragments, $q = 0, 1$, at projectile energies of 1.5, 3.0, and 5.0 keV/amu for $^3$He$^{2+}$ + CH$_2$O.

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