MEASUREMENT OF THE DISTRIBUTIONS
OF
INTERNUCLEAR SEPARATIONS IN 3.0-MeV H$_2^+$ AND 3.63-MeV HeH$^+$ BEAMS

by
Elliot P. Kanter, Patrick J. Cooney, Donald S. Gemmel,
Zeev Vager, Werner J. Pietsch and Bruce J. Zabransky

Prepared for
8th International Conference
on
Atomic Collisions in Solids
Hamilton, Ontario, Canada
August 13-17, 1979

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS
Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.
The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

<table>
<thead>
<tr>
<th>The University of Arizona</th>
<th>The University of Kansas</th>
<th>The Ohio State University</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnegie-Mellon University</td>
<td>Kansas State University</td>
<td>Ohio University</td>
</tr>
<tr>
<td>Case Western Reserve University</td>
<td>Loyola University of Chicago</td>
<td>The Pennsylvania State University</td>
</tr>
<tr>
<td>The University of Chicago</td>
<td>Marquette University</td>
<td>Purdue University</td>
</tr>
<tr>
<td>University of Cincinnati</td>
<td>The University of Michigan</td>
<td>Saint Louis University</td>
</tr>
<tr>
<td>Illinois Institute of Technology</td>
<td>Michigan State University</td>
<td>Southern Illinois University</td>
</tr>
<tr>
<td>University of Illinois</td>
<td>University of Minnesota</td>
<td>The University of Texas at Austin</td>
</tr>
<tr>
<td>Indiana University</td>
<td>University of Missouri</td>
<td>Washington University</td>
</tr>
<tr>
<td>The University of Iowa</td>
<td>Northwestern University</td>
<td>Wayne State University</td>
</tr>
<tr>
<td>Iowa State University</td>
<td>University of Notre Dame</td>
<td>The University of Wisconsin-Madison</td>
</tr>
</tbody>
</table>

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the United States Government.
MEASUREMENT OF THE DISTRIBUTIONS OF INTERNUCLEAR SEPARATIONS IN 3.0-MeV H₂⁺ and 3.63-MeV HeH⁺ BEAMS

ELLIOT P. KANTER, PATRICK J. COONEY, DONALD S. GEMMELL, ZEEV VAGER,
WERNER J. PIETSCH, AND BRUCE J. ZABRANSKY

Argonne National Laboratory, Argonne, Illinois 60439*

Angular distributions of charged dissociation fragments are measured for 3.0-MeV H₂⁺ and 3.63-MeV HeH⁺ ions incident on ~160 Å carbon targets. By using the reflection method for a pure Coulomb potential, we unfold from these data the distributions of internuclear separations for each molecular-ion species prior to dissociation. These results are insensitive to ion-source conditions. For H₂⁺ this distribution, while ~2 times wider than a pure ground vibrational state population, is markedly different from the Franck-Condon distribution that has been previously assumed by other authors with similar r.f. and duo-plasmatron ion sources. For HeH⁺ the distribution is slightly broader (~1.5 times) than that expected for a pure ground state population. From the data, we are able to extract the initial vibrational state population in the incident beam.

* Work performed under the auspices of the Division of Basic Energy Sciences of D.O.E.
When a swiftly moving molecular projectile (one whose velocity, \( V_o \), is large compared with the Bohr velocity \( e^2/h \)) is incident upon a solid target, the more weakly bound electrons (typically, those with orbital velocities less than \( V_o \)) of the projectile can be expected to be stripped off within a few Å of penetration into the target—that is to say, in times of \( \sim 10^{-17} \) sec. This is a consequence of the large cross sections (\( \sim 10^{-16} \) cm\(^2\)/atom) for electron loss due to collisions with target electrons. The projectile continuing into the solid then undergoes a "Coulomb explosion" as the remaining molecular constituents form a cluster of monatomic ions which explode apart under the influence of their mutual Coulomb repulsion. Inside the target, the ions of the cluster will have rapidly fluctuating charges as they pick up and lose electrons. There will, however, be a set of average (non-integral) charges that determine the magnitude of the Coulomb explosion. The Coulomb repulsion inside the target can be assumed to be dynamically screened with a screening distance \( a = V_o/\omega_p \), where \( \omega_p \) is the volume plasma frequency of the target. If the target is a thin enough foil, the cluster will emerge into the vacuum downstream. There is then no further screening and the Coulomb repulsion will continue between ions that now adopt integral charges. For a foil about 100 Å thick, the dwell time of the cluster inside the foil is \( \sim 10^{-15} \) sec. The time for the Coulomb explosion to run its course, converting the initial electrostatic potential energy into kinetic energy of the separating fragments, is also \( \sim 10^{-15} \) sec. By contrast, the times associated with vibrational and rotational motions and with electronic rearrangements of the molecular projectile
are usually long compared with $10^{-15}$ sec. It is therefore a reasonable approximation to assume that the Coulomb explosion commences at the front surface of the foil and that it proceeds thereafter unaffected by any inner molecular motions or rearrangements.

The excess kinetic energy released by the Coulomb explosion produces sizable energy and angle shifts which can be measured in the laboratory distributions of dissociation fragments observed downstream of the target. There are many interesting aspects of the interactions of fast ions with matter that can be explored using molecular-ion projectiles. Recent high-resolution studies on the trajectories of such dissociation fragments, their energy losses, their shifts in angle and energy, their charge states, etc., have produced a wealth of new information on such phenomena as stopping power, radiation damage, and the interactions of fast ions with the plasma oscillations they induce in solids. Studies with foil and gas targets have elucidated many aspects of the differences in interactions in solids and gases 1). The techniques used in these experiments show promise as a tool for studying molecular-ion structures 2).

A central part of the analysis of such experiments is a knowledge of the distribution of internuclear separations contained in the incident molecular ion beam. In most instances, workers have assumed simple distributions centered at the equilibrium separation of the ground electronic state of the ion. The most extensive work has been done for H$_2^+$, where several groups have assumed that direct ionization of the ground electronic and vibrational state of H$_2$ would populate the vibrational levels of H$_2^+$ (1$\sigma_g^+$) according to the Franck-Condon principle 3,4). There are, however, a variety of reasons to expect significantly more complex distributions for the ion source
conditions generally used. Important contributing mechanisms include the
collisional rearrangement of vibrational state populations, autoionization
of high Rydberg states of the neutral molecule and rotational excitation
in the ionizing collision\(^5\). Furthermore, the usual assumption of neutral
molecules being found in the ground vibrational state would appear to be
unfounded in the case of the "hot" ion sources often used for these
experiments.

In order to shed some light on these questions we have conducted
a series of experiments to measure the distribution of initial internuclear
spacings \([D(r)]\) for beams of \(\text{H}_2^+\) and \(\text{HeH}^+\). The basic apparatus used in these
experiments has been described in detail in ref. 1, 6 and 7. This setup
allowed us to measure distributions in angle and energy of the emerging
dissociation fragments with an overall angular resolution of 0.15 milliradians
and relative energy resolution of \(6 \times 10^{-4}\).

Beam energies and target thicknesses were chosen to simultaneously
minimize the influence of both non-equilibrium charge state effects and
multiple scattering. Calculations\(^8\) on the influence of wake forces have
shown that they modify the Coulomb explosion least when the projectile's
internuclear vector is perpendicular to the beam direction. For 3-MeV \(\text{H}_2^+\),
for instance, incident upon a 160-Å carbon foil these calculations show that the
spacings and peak widths in the angular part of a "cross" are modified by
less than 0.5% by wake forces. In the remainder of this section, we
therefore restrict our discussion to the angular part of the crosses and
we neglect wake effects.
In order to extract a $D(r)$ distribution from an angular distribution one needs to deconvolute the non-negligible effects of multiple scattering and (to a lesser extent) of the experimental angular resolution. The deconvolution procedure that we have used for this has been described in ref. 1. Figure 1 shows the result of this unfolding procedure for the case of an $H_2^+$ beam [the abscissa in fig. 1 has been converted from an angle scale to a COM velocity scale]. Because the functional form used for the multiple scattering distribution has a long tail, there is a region corresponding to high COM velocities (near the extreme wings of the data) where the deconvolution is not valid. This translates into a cutoff at small internuclear separations (at about $r = 0.5 \AA$) in the derived distribution $D(r)$.

In our analysis, we assume that in a dissociative collision the molecular projectile makes a sudden electronic rearrangement while leaving its nuclear constituents unperturbed. That is, we consider the projectile as undergoing a sudden vertical transition up to some excited electronic state which then dissociates liberating a total COM kinetic energy of $U(r) - U(\infty)$, where $U(r)$ is the potential energy at an internuclear separation $r$ for the particular final electronic state involved. The relation

$$v = \left(\frac{1}{m_f}\right) \sqrt{2\mu(U(r) - U(\infty))}^{1/2} \tag{1}$$

where $\mu$ is the reduced mass of the projectile, then serves as a mapping function relating the COM velocity of a fragment to the potential and to the initial internuclear separation. For the case of solid targets, $U(r)$ is assumed to be a simple Coulomb potential.
If we now further assume that the cross section for the electronic excitation is independent of the spatial orientation of the projectile and also independent of its internuclear spacing, then we can readily derive the relationship between the distribution functions for \( v \) and \( r \).

\[
G(v) = \frac{1}{(4\pi v^2)^{-1}} D(r) \frac{d}{dv} \quad (2)
\]

where \( v \) and \( r \) are related via eq. (1) and the distribution functions are normalized by

\[
\int_0^\infty D(r) dr = 1 \quad (3)
\]

and

\[
4\pi \int_0^\infty G(v) v^2 dv = 1. \quad (4)
\]

Another way of viewing eq. (2) is simply to note that for fragments whose COM velocities are greater than the limits imposed by our resolution, the contribution of a given \( r \)-value to our measured distributions is spread out over the phase space \( 4\pi v^2 dv \). For a detailed discussion of the validity and limitations of the reflection method see ref. 9.

In this manner, and using a pure Coulomb potential in eq. (1), we have derived the distributions shown in figs. 2 and 3 for \( D(r) \) in \( H_2^+ \) and \( HeH^+ \), respectively. Also shown in each figure is the calculated distribution.
for the ground vibrational and electronic state. For \( \text{H}_2^+ \), where it was thought to be reasonable to assume that the molecular ion is formed by direct ionization of \( \text{H}_2 \) we show additional distributions \( D(r) \) calculated on the basis of \( \text{H}_2^+ \) vibrational populations given by i) the (approximate) Franck-Condon factors of von Busch and Dunn\(^5\), ii) the parameters of Itikawa\(^10\) (these are parameters used in a computation that gives excellent agreement with the observed photoelectron intensities from \( \text{H}_2 \)) and iii) a mixture of \( \text{H}_2^+ \) level populations obtained assuming the initial \( \text{H}_2 \) to be 59% in the ground state and 42% in the first excited vibrational state, using Itikawa's and von Busch and Dunn's population parameters, respectively.

The derived distributions \( D(r) \) show the most probable values of \( \langle r \rangle \) to be 1.17 Å for \( \text{H}_2^+ \) and 0.80 Å for \( \text{HeH}^+ \). These may be compared with values of 1.08 Å and 0.79 Å obtained for the ground states alone in \( \text{H}_2^+ \) and \( \text{HeH}^+ \), respectively. For \( \text{HeH}^+ \) the derived \( D(r) \) is about 1.5 times wider than expected from the ground state alone. This fact, together with the small overall shift of the distribution towards higher \( r \) values, indicates that most of the \( \text{HeH}^+ \) ions are incident in the ground vibrational state with a relatively small fraction in the first one or two vibrationally excited states. For \( \text{H}_2^+ \) on the other hand, excited vibrational levels are clearly much more involved, although the population of these levels is significantly lower than has been assumed by other authors\(^3,4\) in analyzing Coulomb explosion experiments. This difference between the results for \( \text{HeH}^+ \) and \( \text{H}_2^+ \) is not very surprising in view of the very different formation process involved. Since the neutral \( \text{HeH} \) is not stable, \( \text{HeH}^+ \) is formed by ion-molecule ions rather than direct ionization.
We believe that the factors most likely responsible for the deviation of our derived \( D(r) \) for \( \text{H}_2^+ \) from a Franck-Condon-like distribution\(^5\) are firstly, the fact that in the ion source the initial \( \text{H}_2 \) is not always in its ground state and secondly, the higher vibrational states of \( \text{H}_2^+ \) are depleted either in the high-pressure ion-source region or in the accelerator and flight-tube enroute to the target. In the ion-source, the high vibrational states may be preferentially collisionally de-excited and enroute to the target, the now swift ions may have their high vibrational states preferentially dissociated by collisions with residual gas in the vacuum system. We have noted that the results we obtain are not observably dependent upon the ion-source parameters that are presently at our disposal to vary. In addition, autoionization of high Rydberg states and rotational effects may play a role in the ion source\(^5\).

Attempts to correlate vibrational-state populations to our measured radial distributions (Fig. 2c and Fig. 3) are only moderately successful. A histogram of the resulting population for \( \text{H}_2^+ \) is shown in Fig. 4. It is worth noting that our derived distributions can be expected to be in error for internuclear separations large compared with the characteristic electronic screening distance for fast ions traversing carbon. Assuming this distance to be \( a = \frac{v_0}{\omega_p} \), where \( \omega_p \) is the volume plasma frequency of carbon, we obtain \( a = 4.3 \, \text{Å} \) and \( a = 3.0 \, \text{Å} \) for 3.0-MeV \( \text{H}_2^+ \) and 3.63-MeV \( \text{HeH}^+ \), respectively. We have not made any correction for screening effects in our derivation of \( D(r) \).
(such effects would produce a very slight shift to lower r). A possible explanation for our failure to obtain a better fit to a vibrational population may be the presence in the incident beam of bound $H_2^+$ molecules in higher electronic states. This would produce a shift toward somewhat larger internuclear separations.

We have found these measured radial distributions to be quite important in the analysis of $H_2^+$ and $HeH^+$ dissociation in gas; using the proper molecular potentials, these distributions can quite accurately reproduce the shapes of the dissociation spectra.
References


Figure Captions

Fig. 1. Velocity spectrum for outgoing $\text{H}^+$ from the dissociation of 3.0-MeV $\text{H}_2^+$ in a 172-A thick carbon foil. The points are the data, transformed to center-of-mass velocity from a lab angular distribution at zero energy shift. The solid curve results from the deconvolution of multiple scattering from these data, as discussed in Reference 1.

Fig. 2. Radial distribution functions for incident 3.0-MeV $\text{H}_2^+$ ions. The solid curve in (a), (b), and (c) is obtained from the deconvoluted angular distribution given in Fig. 1. In (a), the dashed curve is the radial distribution based on the vibration state distribution derived by von Busch and Dunn from the ionization of the ground-vibrational state of $\text{H}_2$; the chained curve is a similar result based on Itikawa's calculations; the dotted curve is the distribution for the ground-vibrational state of $\text{H}_2^+$ only. In (b), the dotted curve is the radial distribution resulting from ionization of the first excited-vibrational state in $\text{H}_2$, as calculated by von Busch and Dunn, while the dashed curve represents a best fit to our data using a linear combination of the distributions originating from the two lowest-lying vibrational states in $\text{H}_2$. The dotted curve in (c) is a best fit to our data using a linear combination of all 19 vibrational states of the ground-electronic state of $\text{H}_2^+$. 
Fig. 3. Radial distribution function for incident 3.63-MeV HeH$^+$ ions. The points are derived from the data. The solid curve is the best fit to the data, obtained by adjusting the fractional contribution of each of the eleven vibrational levels of the electronic ground state. The chained curve is the distribution for the ground-vibrational state only.

Fig. 4. A histogram of the vibrational-state population of the H$_2^+$ electronic ground state derived from the fit to the radial distribution in Fig. 2b.
Fig. 1

$\text{H}_2^+$ on C
3.0 MeV

COUNTS

PROTON COM VELOCITY ($v/c$)
Fig. 2

INTERNUCLEAR SEPARATION (Å)

PROBABILITY (Å⁻¹)
$H_2^+$ Vibrational State Population

- $P(\nu)$ fit to data
- Franck-Condon
- Photodissociation (von Bush & Dunn)