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14. ABSTRACT

Our research into the chemical properties of highly vibrationally excited molecules has revealed a strong connection between large amplitude vibrational motion and the ability of a molecule to accept or donate electrons. In this proposal, we explain the work leading up to this insight and suggest ways to further test our understanding of this phenomenon. We suggest two experiments to extrapolate these results to completely new kinds of chemical encounters: the vibrational enhancement of electron capture and the direct observation of vibrational promotion of an electron transfer reaction. This work may have significant implications for electron scavenging around re-entry vehicles and accompanying communications blackouts.

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Overview

This document reports on work performed under the grant: F49620-01-1-0193, Air Force Office of Scientific Research, $455,000, Dec. 1, 2000-Nov. 30, 2003. At the outset of the last funding period, our main interest concerned the scattering of highly vibrationally excited molecules from solid surfaces and the microscopic dynamics of such processes. One of our principal results concerns the ability of vibrational motion to promote electron transfer from the metal to the incoming molecule when highly vibrationally excited molecules collide at metal surfaces. An update on our study of vibrational promotion of electron transfer is presented below.

As part of this work we have been motivated to work on new ways of producing intense molecular beams of highly vibrationally excited molecules. To this end we have taken up efforts to transversely refocus molecular beams of highly vibrationally excited molecules using an electric hexapole field. The AFOSR has supported design and construction of a new apparatus in our laboratory that combines stimulated emission pumping of NO, and thereby state-selective optical excitation of highly vibrationally excited molecules, with hexapole focusing. This instrument has now been completed and
recently, we have succeeded in transversely refocusing NO(\nu=18). Our preliminary results are described below.

One of the ongoing objectives of our work has been to find other conditions where vibrational promotion of electron transfer might be important. Specifically, we have begun working toward finding evidence of similar electron transfer dynamics in bimolecular gas-phase collisions. In the course of commissioning a velocity map imaging apparatus for these studies, we have performed experiments on the photochemistry of ClN\textsubscript{3}, which is the commonly used precursor to NCl(\textit{a}^1\Delta), an important energy reservoir compound for the chemical iodine laser. The results were very exciting. Velocity map imaging results on ClN\textsubscript{3} photochemistry provide strong evidence of photochemical production of cyclic-N\textsubscript{3}. These experiments represent the best available evidence that ring formation is possible in an all-Nitrogen molecule.

The remainder of this report is organized as follows. First, we present a list of publications and scientific presentations of the work supported by this grant. A brief review of the important results from our surface scattering and hexapole focusing experiments is presented. Finally, a rather detailed presentation of the new photochemical results on ClN\textsubscript{3} is presented the describes the most exciting work.

**Publications Resulting From This Work**


2. **Vibrational Promotion of electron transfer**, Y. Huang, S.J. Gulding, C.T. Rettner,


Scientific Presentations of the Work Supported by This Grant

1. Invited Lecture, Department of Chemistry Colloquium Series, Emory University, Feb. 10, 2000.


5. Invited Lecture, Department of Chemistry EPFL, Lausanne Switzerland, May 1 2000.

6. Invited Lecture, Department of Physics University of Bielefeld, Bielefeld, Germany May 3, 2000.


8. Invited Lecture, Institute of Atomic and Molecular Science (IAMS), Taipei Taiwan, June 12, 2000

9. Invited Lecture, Synchrotron Radiation Research Center, Hsinchu, Taiwan, June 13, 2000
10. Invited Lecture, CECAM Workshop on Molecular Aspects of Gas Dynamics, Lyon France, June 28


13. Poster Presentation: Gordon Research Conference on Molecular Energy Transfer, 1/14/2001-1/19/2001, Ventura California


17. Invited Speaker, “Physical Chemistry Seminar”, Boston University, Boston Massachusetts, Sept. 16 2002

18. Invited Speaker “Physical Chemistry Seminar”, Massachusetts Institute of Technology, Boston Massachusetts, Sept. 17 2002
19. Invited Speaker “Physical Chemistry Seminar”, University of Sherbrooke, Quebec Canada, Sept. 18 2002

20. Invited Speaker “Physical Chemistry Seminar”, Emory University, Atlanta Georgia, Sept. 20, 2002

21. Invited Speaker “Conference on Stereo-Dynamics of Chemical Reactions” Schoorl, the Netherlands Dec. 1 – 6 2002

22. Invited Colloquium Speaker, University of Leiden, Leiden, the Netherlands Dec. 10, 2002


**Hexapole Focusing and Surface Scattering of Highly Vibrationally Excited NO**

One of the major motivations for our work concerns the properties of highly vibrationally excited Nitric Oxide. This molecule produces an important source of non-thermal infrared radiation in the upper atmosphere that is controlled by molecular interactions in both gas-phase bimolecular and molecule-surface collisions. Because this
molecule is found far out of local thermodynamic equilibrium, it is necessary to understand its vibrational state-specific dynamics. We have in the past worked hard to understand bimolecular gas-phase collisions involving highly vibrationally excited NO. More recently we have focused on collisions of highly vibrationally excited NO with solid surfaces.

*Electron Mediated Vibrational Energy Transfer at Metal Surfaces*¹

One of the most significant results of our work is the observation of efficient multi-quantum vibrational relaxation of NO(ν=15) in specular collisions with a gold surface. See Fig. 1. This has been explained by vibrational promotion of electron transfer. In this picture, large amplitude vibrational motion strongly influences electron transfer dynamics as the stretched NO bond may easily accept electrons, while the compressed NO bond repels them (Fig. 2). This enables the stretched NO molecule to accept an electron near the Fermi-level of the metal and upon bond compression deliver it back to the metal at a far higher energy converting large amounts of NO-vibration to metal-electron excitation. These insights have lead us to carry out experiments that probe more deeply models of electron mediated vibrational energy transfer. In two studies we have carried out experiments that push the limits of the present model of vibrational excitation of molecules at metal surfaces.

In the first, measurements of vibrational excitation and de-excitation of NO(ν=2) scattering from a Au(111) surface showed that the probability of both processes increases strongly with the kinetic energy of the incident NO. This qualitative result is consistent with a vibrational energy transfer mechanism involving electron-hole pairs but not with

¹ See the publication list: #1–#5.
competing adiabatic models. The form of the energy dependence and other features of the measurements, are however not quantitatively in accord with existing calculations.

In the second study, we reported the surface temperature dependence for \( \Delta v=+1 \) vibrational excitation of NO(\( v=2 \)) due to collisions with Au(111) at two incidence energies. This was compared to previous measurements on Ag(111) and Cu(110). The standard model for electron-hole pair mediated vibrational excitation predicts that all three metals will exhibit a nearly Arrhenius temperature dependence with the same effective activation energy. While scattering on Ag(111) and Cu(110) obey this prediction, our new results show that the temperature dependence is non-Arrhenius on Au(111).

We suggested that the large spin-orbit interaction present for Au(111) surface electronic states may be important for vibrational excitation. These experiments indicate that the simple bulk electronic structure models of the dynamics of vibrational energy transfer at metals may be too simple.

\textit{Vibrational Energy Transfer at Insulators}^{2}

To compare the behavior on metals to that on insulators, we have made measurements of the vibrational survival probability of NO(\( v=12 \)) suffering collisions with a LiF(001) crystalline surface. Survival probabilities are near unity in all cases, showing the key observation associated with vibrational promotion of electron transfer is absent on an insulator. At the lowest reported incidence energies (5.3 kJ/mol) and surface temperatures (290K), vibrational relaxation is enhanced, scattering angular distributions approach Cos(\( \theta \)) and rotational temperatures of the scattered molecules approach the
surface temperature. At higher incidence energies, rotational temperatures are higher than
the surface temperature and angular distributions narrow approaching \( \cos^6 \theta \). These
results suggest that trapping/desorption is occurring at least at the lowest incidence
energies and surface temperatures. Substantial vibrational relaxation appears to occur
when residence time are as small as a few ps. This is many orders of magnitude faster
than has been reported for diatomic molecules relaxing from \( v=1 \) on salt crystals. These
experiments suggest that theoretical work is still needed to help us understand the
vibrational relaxation of highly vibrationally excited molecules at insulator surfaces.

**Hexapole Focusing of NO(\( v=18 \))\(^{3}\)**

We have also obtained AFOSR support to develop a new means of producing
highly vibrationally excited molecules in a molecular beam. This approach takes
advantage of the state-specific nature of hexapole focusing and exploits this in
combination with optical preparation of highly vibrationally excited NO. We have
recently carried out experiments where hexapole focusing is combined with stimulated
emission pumping in a molecular beam, providing control over the molecule’s ro-
vibronic quantum numbers, its laboratory frame velocity and its transverse divergence.
Hexapole focusing profiles can be quantitatively reproduced by classical trajectory
simulations. These experiments provide new ways of manipulating beams of
vibrationally excited molecules including: 1) transverse refocusing and concomitant
improved efficiency for transport of the vibrationally excited molecules, 2) relative
enrichment of the concentration of the vibrationally excited molecules with respect to the

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\(^2\) See the publication list: #6.
\(^3\) See the publication list: #7.
unexcited portion of the beam and, 3) orientation of vibrationally excited molecules. See
Fig. 3.

The remainder of this report concerns velocity map imaging investigations into
the photochemistry of ClN₃. This work has led us to conclude that ClN₃ is a
photochemical precursor to cyclic-N₃, which will be the focus of the next funding period.
Thus the following sections serve to introduce the topic of cyclic-N₃ production as well
as present our prior results.

Production of Cyclic-N₃: Velocity Map Imaging of ClN₃ Photochemistry

Overview of ClN₃ Photochemistry

Using a new velocity map imaging apparatus developed under the support of the AFOSR,
we (in collaboration with Prof. Michael Heaven⁴ of Emory University) have recently
carried out the first collision-free experiments on the ultraviolet photochemistry of
chlorine-azide (ClN₃). We have studied three photochemical channels:

\[
\text{ClN}_3 + h\nu \rightarrow \text{Cl} + \text{N}_3 \quad \quad (R1)
\]

\[
\text{ClN}_3 + h\nu \rightarrow \text{NCl}(a^1\Delta \text{ or } X^3\Sigma) + \text{N}_2 \quad \quad (R2)
\]

\[
\text{ClN}_3 + 2 \text{hv} \rightarrow \text{NCl}^+ + \text{N}_2 + e^- \quad \quad (R3)
\]

Recent interest in the photochemistry of chlorine azide (ClN₃) derives from
demonstrations that the primary photoproduct NCl(\(a^1\Delta\)) can be used as an effective
energy carrier in chemical iodine lasers, a topic of significant relevance to the AFOSR

⁴ See the publication list: #8 – #11.
⁵ Professor Heaven and Dr. Anatoly Komissarov spent about two weeks teaching us the use of the ClN₃
generator used to form molecular beams of this molecule and after returning to Atlanta have been very
mission (1-3). This stimulated several past studies of the near UV photolysis of ClN₃, in particular by Dehnicke et al. (4), Coombe and co-workers (5-9), Henshaw et al. (10), and Komissarov et al. (11, 12).

Despite substantial effort, basic features of this chemistry still had not been established prior to our work. For example, the thermochemistry of the two most important reactions used to form NCl(1Δ):

\[
\text{ClN}_3 + \text{hv} \rightarrow \text{NCl} \left(1\Delta \text{ or } X^3\Sigma^-\right) + \text{N}_2 \quad \text{(R2)}
\]

\[
\text{Cl} + \text{N}_3 \rightarrow \text{NCl} \left(1\Delta \text{ or } X^3\Sigma^-\right) + \text{N}_2 \quad \text{(R4)}
\]

remained unclear, as did the singlet/triplet branching ratio for both reactions. In our experiments, we were able to obtain the maximum release of translational energy from the velocity map image of recoiling REMPI-detected N₂ in reaction R2. This allowed us to obtain an accurate experimental value for this reaction’s thermochemistry⁶ and led to a measure of the singlet/triplet branching ratio for reaction R2 (13) that supported prior experiments done under collisional conditions (12).

Velocity map imaging experiments on all of the products of reaction R3 led to accurate thermochemistry for this reaction. Through knowledge of the ionization potentials of NCl (14) and ClN₃ (15) an independent determination of the thermochemistry of reaction R2 was also possible. The two independent experiments were in quantitative agreement with one another on the 0.1 eV level of accuracy. The

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helpful in performing some theoretical calculations and performing some complementary experiments not described in this report.

⁶ The mechanics of this kind of analysis is presented in more detail below when we come to a consideration of the evidence supporting the photochemical production of cyclic-N₂.
latter work also provided a detailed look at the dynamics of the decomposition of the unstable $\text{ClN}_3^+$ ion (16).

By deriving the maximum release of translational energy for Cl-atoms recoiling from reaction R1, we were likewise able to experimentally determine the bond energy, $D_0(\text{Cl–N}_3)$, (17, 18). This thermochemistry could be combined with the thermochemistry of reaction R2 to obtain accurate thermochemistry of the second important $\text{NCl}(a^1\Delta)$ forming reaction R4.

The results of our new experiments, together with past work now provides accurate (within 0.1 eV) thermochemistry for all molecules containing one Cl-atom and three Nitrogen-atoms, providing a better foundation for understanding the chemistry of $\text{NCl}(a^1\Delta)$. The derived thermochemistry is summarized in Fig. 4.

**Photochemical Production of Cyclic-$\text{N}_3$**

In the course of these studies, we discovered what is certainly the most significant result of the last funding period, both from a fundamental point of view and from the point of view of AFOSR mission. **Our experiments provide strong evidence that ClN$_3$ is a photochemical precursor of the simplest all-Nitrogen cyclic molecule, cyclic-N$_3$**.

For Nitrogen unlike most elements, the energy of an N–N single bond is substantially less than one-third, and the energy of an N=N double bond is substantially less than two-thirds of an N≡N triple bond. Consequently, all-Nitrogen species that form rings at the expense of multiple bonds are subject to a strong chemical driving force toward dissociation to N$_2$. 
\[
\text{N}_2 \xrightarrow{\Delta H \ll 0} \text{N}_2 + \text{N}
\]

Not surprisingly, the ability of Nitrogen to form cyclic structures has been difficult to verify. Several experiments have led to the postulate of a cyclic poly-nitrogen species; but these have either remained unconfirmed or later been disproved (19-22). Recently, the stabilization energy of an ionic crystal was exploited, allowing production of $\text{N}_5^-$ in an ionic salt (23). Still the possible existence of isolated cyclic all-Nitrogen allotropes has remained largely a topic for theory (22, 24-41) and the question of how such molecules might be produced in the laboratory has remained unanswered (42).

Partly due to the fact that this class of molecules is so unstable, they have been vigorously sought as materials capable of storing large amounts of energy in minimal volumes, so-called “high energy and density materials” (43). Their natural tendency to decompose to $\text{N}_2$ also makes them high on the list of environmentally friendly explosives and propellants.

The most studied example, tetraazahedrane (19, 22, 24, 25, 28-35) better known as tetrahedral Nitrogen, molecule (1), is illustrative of the chemical properties of this family of molecules.

![Molecule (1)](image)

Formally in compliance with the octet-rule, it is a closed shell-species of singlet spin-multiplicity (24) that may release more than 760 kJ/mole by decomposition to 2 $\text{N}_2$ (22,
28). Theory shows that the barrier to decomposition to ground state \( \text{N}_2 \) is greater than 250 kJ/mole, strongly suggesting that it is an isolable molecule (28, 30). However, decomposition via "spin-forbidden" curve-crossings forming electronically excited products, which is predicted to occur over a smaller barrier (31), may lower the stability of molecule (1). Molecule (1), like all other gas-phase cyclic poly-N molecules, has yet to be observed (19, 22).

The simplest all-Nitrogen allotrope from which a ring can be formed is \( \text{N}_3 \) (25-27). Recent high-level calculations (25) predict a \( \text{C}_{2v} \) molecule of \( \text{B}_1 \) symmetry and doublet spin-multiplicity with two long (1.455 Å) and one short (1.218 Å) N/N bonds (44), molecule (2).

![Molecule 2](image)

**Molecule (2)**

Isomerization to the well-known linear isomer (the azide radical) is predicted to be exoergic by 125 kJ/mole, spin-allowed but limited by a 140 kJ/mole barrier (25). Dissociation to ground state \( \text{N}(^4\text{S}_{3/2}) \) and \( \text{N}_2 \left( X^1\Sigma^+_g \right) \) is exoergic by \( \sim 125 \) kJ/mole, but spin-forbidden (25). The lowest energy spin-allowed dissociation forms \( \text{N}(^2\text{D}) \) and \( \text{N}_2 \left( X^1\Sigma^+_g \right) \) and is endoergic by \( \sim 96 \) kJ/mole (25). Theoretical calculations also suggest that cyclic-\( \text{N}_3 \) may undergo barrierless exoergic recombination with \( \text{N}(^2\text{D}) \) to form tetrahedral \( \text{N}_4 \) (25). This makes cyclic-\( \text{N}_3 \) one of the only suggested precursors to tetrahedral \( \text{N}_4 \) (39).
In the course of these studies, we have measured accurate velocity maps of Cl-atoms formed in reaction R1. Like photoelectron spectroscopy where the translational energy distribution of the electron reveals quantum-level structure of the simultaneously formed ion, velocity-map images of quantum-state-selected Cl-atoms recoiling from photolyzed ClN₃ reveal a medium resolution energy spectrum of N₃. These experiments indicate the presence of a low-lying excited state of N₃ at 1.35 ± 0.1 eV, which compares well with recent theoretical predictions of the energy of cyclic-N₃, molecule (2) (25).

Fig. 5a shows the observed velocity map image of ground-state Cl-atoms produced in reaction (R1). Here, the direction of the ClN₃ molecular beam is out of the plane of the paper pointing directly at the reader. The polarization direction of the laser light beam is also indicated (ê). The position at which a Cl⁺ ion is detected in the image reflects the velocity (both direction and speed) of the recoiling Cl-atom from which it was formed.

One will immediately notice that there is a limiting speed (indicated by the dotted circle) beyond which no Cl-atoms are detected. This limit is found when the maximum possible fraction of the absorbed photon energy beyond that required to break the N-Cl bond in ClN₃ is channeled into translational energy of the photoproducts, leaving N₃ with a minimum of internal energy. This limiting velocity provides a means of obtaining an upper limit to the N-Cl bond energy in ClN₃, D₀(Cl-N₃). It can be shown that this velocity is given by Eq. (1).

$$v_{Cl}^{MAX} \leq \sqrt{\frac{\hbar v - D_0(Cl-N₃)}{m_{Cl}(m_{N₃}+m_{Cl})} \frac{2m_{N₃}}{m_{Cl}}} \quad Eq. (1)$$

where, $\hbar v$ is the energy of the photon absorbed by ClN₃
and \( D_0(\text{Cl}-\text{N}_3) \) is the N-Cl bond energy.

The vast majority of the photodissociation events, where some internal energy appears in the \( \text{N}_3 \) photofragment, appear well within the dotted circle. Also visible in Fig. 5a is a second limiting speed (indicated by the dashed circle) beyond which \textit{many} Cl-atoms are never formed. Since only a single quantum state of the Cl-atoms are detected with REMPI, this indicates that the internal energy distribution of the \( \text{N}_3 \) photofragment is markedly bimodal.

To analyze this quantitatively, we derived the velocity and angular distributions of the Cl-atoms from an inverse-Abel transform of the image of Fig. 5a (45). The corresponding translational energy distribution of the recoiling Cl-atoms is shown in Fig. 5b. One sees now clearly the translational energy cut-off at a Cl-atom translational energy of 1.65 eV. We may use Eq. (1) to obtain Eq. (2) below:

\[
D_0(\text{Cl} - \text{N}_3) \leq \frac{\hbar}{2} m_{\text{Cl}} \left( v_{\text{Cl}}^{\text{MAX}} \right)^2 \frac{m_{\text{N}_3} + m_{\text{Cl}}}{m_{\text{N}_3}} \quad \text{Eq. (2)},
\]

and derive the dissociation energy of ClN\(_3\), \( D_0(\text{Cl}-\text{N}_3) = 2.24 \pm 0.1 \) eV, which is in agreement with other thermodynamic quantities (46-49), in particular the ClN\(_3\) heat of formation. This shows that the fastest detected Cl-atoms correspond to formation of the linear azide radical with little or no internal excitation.

In a way reminiscent of photoelectron spectroscopy, it is useful to realize that the Cl-atom translational energy distribution shown in Fig. 5b is likewise a medium resolution energy spectrum of the \( \text{N}_3 \) fragment formed in the photodissociation or ClN\(_3\). By the principle of energy conservation, low translational-energy Cl-atoms directly correspond to high internal energy \( \text{N}_3 \) radicals. To make this clear, the upper x-axis of Fig.5b shows how the measurement reflects the \( \text{N}_3 \) internal energy distribution. The most
remarkable observation of this work is the bimodal nature of this distribution, with the origins of the two components appearing at 1.65 and 0.9 eV in Cl-atom translational energy space, respectively. Alternatively, one may state that the origins of the two components appear at 0.0 and 1.35 eV internal energy of the N₃ molecule, the first of which is assigned to the linear azide radical.

An energy gap of 1.35 eV would normally be attributed to electronic excitations in a molecule; however, there is no experimental evidence of an excited electronic state of the well-studied linear azide N₃ lying 1.35 eV above the ground state. Extensive spectroscopic studies have revealed the presence of an excited state of 2Σ-symmetry at 4.5 eV (50) and theoretical work shows that the lowest linear quartet is also at about 4.4 eV (27). Recently, the electronic structure of N₃ has been investigated in more depth using quantum chemical methods (25). This study has shown that the experimentally observed 2Σ-state is the lowest lying excited doublet electronic state with a linear structure and the calculated energy is in good agreement with experiment (50). These same theorists also predict that the lowest excited electronic state of N₃ is a ring structure, belonging to the C₂ᵥ-point group and possessing 2B₁ symmetry, molecule (2). At the highest levels of theory, these authors found the excitation energy to this state (which is the cyclization energy of N₃) to be 1.35 ± 0.05 eV (25). This is shown as the red bar in Fig. 5b. The good agreement with the derived origin of the high energy component of the N₃ excitation distribution is compelling evidence that cyclic-N₃ is formed in the ultraviolet photochemistry of ClN₃.

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7 Preliminary theoretical calculations from Morokuma’s group give no evidence of a bimodal vibrational energy distribution in the N₃ fragment, a result that would be in any event quite surprising.

8 This includes a zero-point energy correction.
References

44. Recent and still unpublished calculations from Morokuma’s group suggest that there may be another nearly isoenergetic ring isomer of 2A2 symmetry
Figure 1. Measured vibrational distribution of NO resulting from scattering of a) NO(v=15) from Au(111) at $E_{\text{incident}}=0.05$ eV and b) NO(v=12) from LiF at $E_{\text{incident}}=0.4$ eV. The remarkable multi-quantum vibrational relaxation seen on the metal has been explained in terms of vibrationally mediated electron transfer. From Y. H. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, Science 290, 111-114 (2000).
Figure 2: Ab initio calculations of NO and NO\(^{-}\), showing the energetic constraints on electron transfers. The inset shows the difference between the two potential curves, the vertical electron binding energy. The positions of the inner and outer extrema of the NO \(v=15\) vibrational wave function are shown with vertical arrows labeled (\(r_\sigma\) and \(r_π\)). The position of the NO potential minimum is shown as \(r_e\). This shows that the energetics of electron transfer depend strongly on the bond length. From Y. H. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **290**, 111-114 (2000).
FIG. 3 Hexapole focusing curves for NO molecules pumped by stimulated emission pumping compared to ground state Molecules: (a) $|v=18, J=1/2, \Omega=1/2\rangle$, (b) $|v=18, J=3/2, \Omega=3/2\rangle$ and (c) $|v=0, J=1/2, \Omega=1/2\rangle$. Data is shown as open squares. The solid black lines are a classical trajectory simulation that quantitatively reproduces the data. The grey lines in (b) are the $M = 1.5$ and $0.5$ magnetic sub-level components. This result demonstrates how optically prepared molecules delivered to an $\Omega=3/2$ level can be made to focus at a much lower voltage than the initially unexcited sample. Also shown as an inset is a polar plot of the oriented $|v=18, J=3/2, \Omega=3/2, M=3/2\rangle$ state of NO prepared at 8 kV Rod Voltage.
Figure 4: Zero Kelvin standard heats of formation (in eV) for molecules that may be constructed from a Cl-atom and three N-atoms. Constructed from recent velocity map imaging results together with past work. The bold underlined values indicate previously well-established heats of formation. The double headed arrows represent well-known thermodynamic transformations. The dashed, single-headed arrows represent thermodynamic transformations observed in our work. In addition, we have observed two-photon ionization (reaction R3) which adds redundant confirmation of these thermodynamics.
Figure 5: (a) Velocity map image of ground state Cl(2P\textsubscript{3/2}) recoiling from ClN\textsubscript{3}. The outer ring records Cl-atoms formed with linear azide radical with little internal energy. The inner ring records Cl-atoms formed with N\textsubscript{3} in an excited state. (b) The translational energy distribution for ground state Cl(2P\textsubscript{3/2}) derived from the velocity map image. The maximum release of translational energy is limited by the N-Cl bond strength in ClN\textsubscript{3}. This translational energy is indicated at 1.65 eV. At this Cl-atom translational energy, N\textsubscript{3} is formed with negligible internal excitation. Slower moving Cl-atoms reflect formation of more internally excited N\textsubscript{3}. The N\textsubscript{3} excitation energy can be read from upper x-axis. The analogy with photoelectron spectroscopy is obvious. The double headed arrow marked “cyclic N\textsubscript{3}” shows where a new feature of the Cl-atom energy spectrum appears reflecting formation of an excited form of N\textsubscript{3}. The most recent theoretical predictions of the cyclization energy of N\textsubscript{3} are shown as the red bar. See text.