Dynamics of Small, Ultraviolet-excited ICN^- Cluster Anions

Amanda S. Case, Anne B. McCoy, and W. Carl Lineberger

SUPPORTING INFORMATION

Figure S1. Total transition moment as a function of angle for fixed R: R = R_{eq} = 3.27 Å.

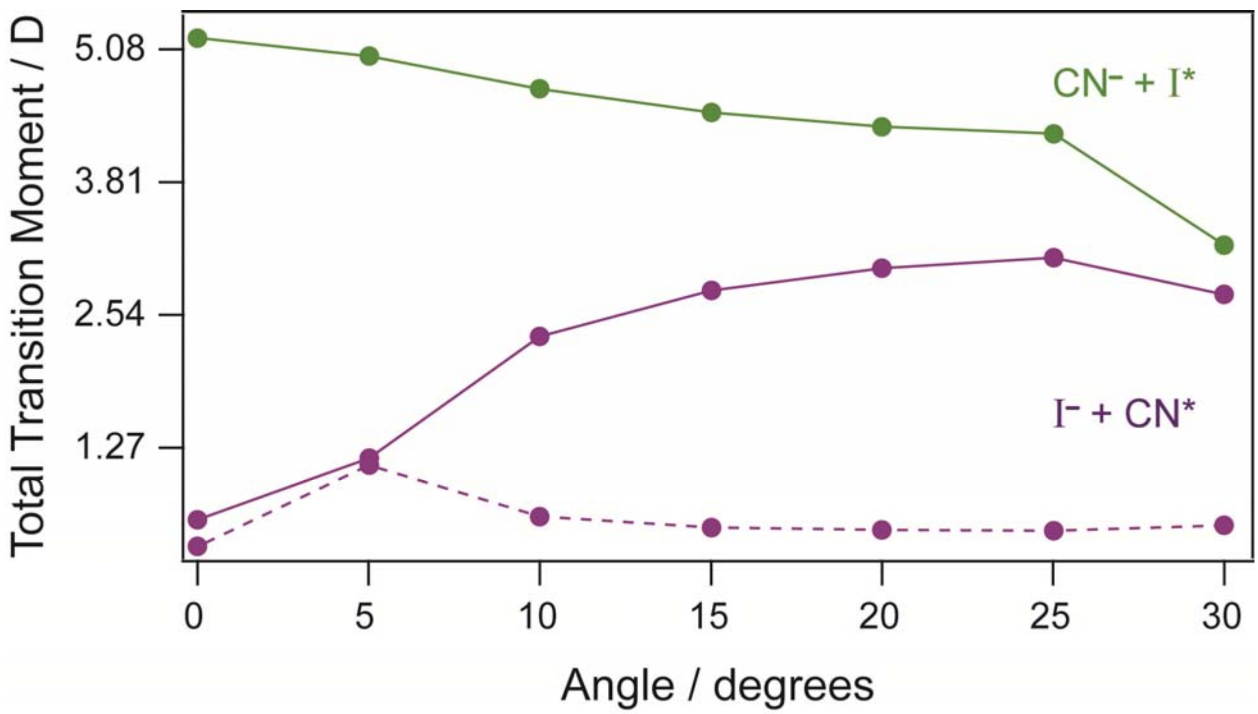

Table S1. Photoproduct branching percentages for ICN^-Ar_n, n = 0–5. The branching percentage of each product shown is the average of 20 data sets, and the value in parentheses displays the standard deviation in the percentage of the given photoproduct over these 20 data sets. The total percentage of ICN^--based photoproducts, I^--based photoproducts, and CN^--based photoproducts are displayed in bold face for each parent ion.

Parent Ion	**ICN^- Products**	**I^- Products**	**CN^- Products**
ICN^-	 **Total = 0%**	I^- 76% (2.82) **Total = 76%**	CN^- 24% (2.82) **Total = 24%**
ICN^-Ar	 **Total = 0%**	I^- 38% (3.70) I^-Ar 43% (3.81) **Total = 81%**	CN^- 19% (3.22) **Total = 19%**
ICN^-Ar_2	ICN^- 3% (0.64) **Total = 3%**	I^- 21% (1.58) ICN^-Ar 48% (2.36) ICN^-Ar_2 11% (2.90) **Total = 80%**	CN^- 17% (3.12) **Total = 17%**
ICN^-Ar_3	ICN^- 2% (0.58) ICN^-Ar 2% (0.73) **Total = 4%**	I^- 15% (1.35) ICN^-Ar 35% (2.67) ICN^-Ar_2 31% (3.46) **Total = 81%**	CN^- 15% (2.83) **Total = 15%**
ICN^-Ar_4	ICN^- 1% (0.64) ICN^-Ar 2% (0.60) **Total = 3%**	I^- 13% (1.22) ICN^-Ar 28% (2.05) ICN^-Ar_2 35% (2.94) ICN^-Ar_3 11% (3.70) **Total = 87%**	CN^- 10% (2.05) **Total = 10%**
ICN^-Ar_5	ICN^- 1% (0.24) ICN^-Ar 1% (0.40) **Total = 2%**	I^- 11% (1.08) ICN^-Ar 22% (1.61) ICN^-Ar_2 33% (2.73) ICN^-Ar_3 22% (1.78) ICN^-Ar_4 2% (1.34) **Total = 90%**	CN^- 8% (1.60) **Total = 8%**

Table S2. Photoproduct branching percentages for $ICN^{-}(CO_2)_n$, n = 0–5. The branching percentage of each product shown is the average of 20 data sets, and the value in parentheses displays the standard deviation in the percentage of the given photoproduct over these 20 data sets. The total percentage of ICN^{-}-based photoproducts, I^{-}-based photoproducts, and CN^{-}-based photoproducts are displayed in bold face for each parent ion.

Parent Ion	ICN^{-} Products	I^{-} Products	CN^{-} Products
ICN^{-}	**Total = 0%**	I^{-} 76% (2.82) **Total = 76%**	CN^{-} 24% (2.82) **Total = 24%**
$ICN^{-}(CO_2)$	**Total = 0%**	I^{-} 82% (1.43) **Total = 82%**	CN^{-} 18% (1.43) **Total = 18%**
$ICN^{-}(CO_2)_2$	**Total = 0%**	I^{-} 39% (1.71) $I^{-}(CO_2)$ 42% (1.62) **Total = 81%**	CN^{-} 18% (1.22) $CN^{-}(CO_2)$ 1% (0.26) **Total = 19%**
$ICN^{-}(CO_2)_3$	ICN^{-} 1% (0.86) **Total = 1%**	I^{-} 28% (2.92) $I^{-}(CO_2)$ 46% (5.77) **Total = 74%**	CN^{-} 20% (5.95) $CN^{-}(CO_2)$ 5% (2.00) **Total = 25%**
$ICN^{-}(CO_2)_4$	ICN^{-} 4% (0.93) **Total = 4%**	I^{-} 18% (1.62) $I^{-}(CO_2)$ 39% (2.57) $I^{-}(CO_2)_2$ 4% (0.81) **Total = 61%**	CN^{-} 17% (3.51) $CN^{-}(CO_2)$ 18% (2.32) **Total = 35%**
$ICN^{-}(CO_2)_5$	ICN^{-} 9% (2.55) **Total = 9%**	I^{-} 7% (1.80) $I^{-}(CO_2)$ 29% (5.14) $I^{-}(CO_2)_2$ 6% (2.08) **Total = 42%**	CN^{-} 13% (4.67) $CN^{-}(CO_2)$ 33% (5.20) $CN^{-}(CO_2)_2$ 3% (1.39) **Total = 49`%**

Energetic Breakdown for Recombination in UV-excited $ICN^{-}Ar_n$

A simple hard-sphere model that only considers translational degrees of freedom is used to describe the kinematics of dissociation for $ICN^{-}Ar_n$. The photodissociation of ICN^{-} and the elastic collinear collision of the CN fragment with an Ar atom are considered as two separate actions. Because only the collinear geometry is evaluated, the numbers given in this section represent the maximum translational energy transfer to the Ar atom.

Excitation of ICN^{-} with a 4.1-eV photon populates two surfaces on which the anion can potentially be trapped, the $^2\Pi_{1/2}$-(A) excited state and the $^2\Pi$-(C) excited states. The $^2\Pi_{1/2}$-(A) excited state has a potential well that is roughly 0.27 eV deep, and in the asymptotic limit there is roughly 2.47 eV of excess energy in this state. Upon dissociation, roughly 2.05 eV of the excess energy goes into translation of the CN fragment; subsequent collision with an Ar atom transfers 0.81 eV into translation of the Ar atom. The argon atom leaves the system along with 0.86 eV of energy (0.81 eV in translation and 0.05 eV from solvent loss). There is the loss of another 0.07 eV due to the translation of the center of mass of the [I^{-}–CN] system and another 0.05 eV because there is always at least one additional solvent atom lost. A simple look at the energetics shows that there is still 1.49 eV of energy in the [I^{-}–CN] system on the $^2\Pi_{1/2}$-(A) excited state. Even with roughly 1.11 eV of energy going into rotation of the CN fragment, trapping is unlikely to occur.

The $^2\Pi$-(C) excited state has a potential well that is roughly 0.1 eV deep, and in the asymptotic limit there is roughly 1.32 eV of excess energy in this state. Upon dissociation, roughly 1.09 eV of the excess energy goes into translation of the CN fragment; subsequent collision with an Ar atom transfers 0.44 eV into translation of the Ar atom. The argon atom leaves the system along with 0.49 eV of energy (0.44 eV in translation and 0.05 eV from solvent loss). There is the loss of another 0.04 eV due to the translation of the center of mass of the [I^{-}–CN] system and another 0.05

eV because there is always at least one additional solvent atom lost. A simple look at the energetics shows that there is still 0.74 eV of energy in the [I^-–CN] system on the $^2\Pi$-(C) excited state. Even with roughly 0.44 eV of energy going into rotation of the CN fragment, we again find that trapping is not likely to occur in this fashion.

There is also the possibility of exciting one or two quanta of CN stretching vibration in the $^2\Pi$-(C) excited state. For v = 1, the excess energy is reduced to about 1.06 eV and a similar analysis finds 0.58 eV of energy in the [I^-–CN] system on the $^2\Pi$-(C) excited state, of which about 0.35 eV should be stored in CN rotation. For v = 2, the excess energy is now about 0.80 eV leaving 0.41 eV of energy in the [I^-–CN] system on the $^2\Pi$-(C) excited state, about 0.26 eV of which will be tied up in CN rotation. While these numbers do not strictly imply trapping on the $^2\Pi$-(C) excited state, population of the ICN^- bending vibration should result in an increase in the fraction of the excess energy stored in rotation of the CN moiety and, thus, point to a plausible mechanism by which recombination occurs following 4.1-eV excitation of ICN^-.