Supplementary Information

Table SI1: Exoergicities of reaction pathways for the reaction $CH_2CN^{2+} + N_2 \rightarrow CH_2CN^+ + N_2^+$, calculated from literature values.[1,2] N_2 is assumed to be in its ground state, $X^1\Sigma_g^+$. Highlighted in bold are the pathways with exoergicities between 3 eV and 7.5 eV, the energy range of the bulk of the experimental exoergicity signals. See article text for details.

Reactant (CH_2CN^{2+}) states	**Product states**		**Total exoergicity**
CH_2CN^{2+} state, relative to the ground state of CH_2CN	N_2^+ state, relative to the ground state of N_2, ($X^1\Sigma_g^+$)	CH_2CN^+ state, relative to the ground state of CH_2CN	Reactant states – total product states
2LD, 30.395 eV	**$X^2\Sigma_g^+$, 15.58 eV**	**1LM, 10.07 eV**	**4.745 eV**
2LD, 30.395 eV	**$A^2\Pi_u$, 16.69 eV**	**1LM, 10.07 eV**	**3.6324 eV**
2LD, 30.395 eV	$B^2\Sigma_u^+$, 18.75 eV	1LM, 10.07 eV	1.574 eV
2LD, 30.395 eV	$D^2\Pi_g$, 22.02 eV	1LM, 10.07 eV	-1.695 eV
2LD, 30.395 eV	$C^2\Sigma_u^+$, 23.58 eV	1LM, 10.07 eV	-3.258 eV
2LD, 30.395 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	1LM, 10.07 eV	-4.0071 eV
2LD, 30.395 eV	$X^2\Sigma_g^+$, 15.58 eV	3LM, 12.11 eV	2.705 eV
2LD, 30.395 eV	$A^2\Pi_u$, 16.69 eV	3LM, 12.11 eV	1.5924 eV
2LD, 30.395 eV	$B^2\Sigma_u^+$, 18.75 eV	3LM, 12.11 eV	-0.466 eV
2LD, 30.395 eV	$D^2\Pi_g$, 22.02 eV	3LM, 12.11 eV	-3.735 eV
2LD, 30.395 eV	$C^2\Sigma_u^+$, 23.58 eV	3LM, 12.11 eV	-5.298 eV
2LD, 30.395 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	3LM, 12.11 eV	-6.0471 eV
4LD, 32.73 eV	**$X^2\Sigma_g^+$, 15.58 eV**	**3LM, 12.11 eV**	**5.04 eV**
4LD, 32.73 eV	**$A^2\Pi_u$, 16.69 eV**	**3LM, 12.11 eV**	**3.9274 eV**
4LD, 32.73 eV	$B^2\Sigma_u^+$, 18.75 eV	3LM, 12.11 eV	1.869 eV
4LD, 32.73 eV	$D^2\Pi_g$, 22.02 eV	3LM, 12.11 eV	-1.4 eV
4LD, 32.73 eV	$C^2\Sigma_u^+$, 23.58 eV	3LM, 12.11 eV	-2.963 eV
4LD, 32.73 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	3LM, 12.11 eV	-3.7121 eV
2CD, 28.88 eV	$X^2\Sigma_g^+$, 15.58 eV	1CM, 11.03 eV	2.270656 eV
2CD, 28.88 eV	$A^2\Pi_u$, 16.69 eV	1CM, 11.03 eV	1.158056 eV
2CD, 28.88 eV	$B^2\Sigma_u^+$, 18.75 eV	1CM, 11.03 eV	-0.90034 eV
2CD, 28.88 eV	$D^2\Pi_g$, 22.02 eV	1CM, 11.03 eV	-4.16934 eV
2CD, 28.88 eV	$C^2\Sigma_u^+$, 23.58 eV	1CM, 11.03 eV	-5.73234 eV
2CD, 28.88 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	1CM, 11.03 eV	-6.48144 eV
2CD, 28.88 eV	$X^2\Sigma_g^+$, 15.58 eV	3CM, 12.87 eV	0.430322 eV
2CD, 28.88 eV	$A^2\Pi_u$, 16.69 eV	3CM, 12.87 eV	-0.68228 eV
2CD, 28.88 eV	$B^2\Sigma_u^+$, 18.75 eV	3CM, 12.87 eV	-2.74068 eV
2CD, 28.88 eV	$D^2\Pi_g$, 22.02 eV	3CM, 12.87 eV	-6.00968 eV
2CD, 28.88 eV	$C^2\Sigma_u^+$, 23.58 eV	3CM, 12.87 eV	-7.57268 eV
2CD, 28.88 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	3CM, 12.87 eV	-8.32178 eV
4CD, 32.94 eV	**$X^2\Sigma_g^+$, 15.58 eV**	**3CM, 12.87 eV**	**4.490322 eV**
4CD, 32.94 eV	**$A^2\Pi_u$, 16.69 eV**	**3CM, 12.87 eV**	**3.377722 eV**
4CD, 32.94 eV	$B^2\Sigma_u^+$, 18.75 eV	3CM, 12.87 eV	1.319322 eV
4CD, 32.94 eV	$D^2\Pi_g$, 22.02 eV	3CM, 12.87 eV	-1.94968 eV
4CD, 32.94 eV	$C^2\Sigma_u^+$, 23.58 eV	3CM, 12.87 eV	-3.51268 eV
4CD, 32.94 eV	$C^2\Sigma_u^+$ $v = 3$, 24.33 eV	3CM, 12.87 eV	-4.26178 eV
2ID, 29.36 eV	**$X^2\Sigma_g^+$, 15.58 eV**	**1IM, 10.25 eV**	**3.536542 eV**
2ID, 29.36 eV	$A^2\Pi_u$, 16.69 eV	1IM, 10.25 eV	2.423942 eV
2ID, 29.36 eV	$B^2\Sigma_u^+$, 18.75 eV	1IM, 10.25 eV	0.365542 eV

2ID, 29.36 eV	$D^2\Pi_g$, 22.02 eV	1IM, 10.25 eV	-2.90346 eV
2ID, 29.36 eV	$C^2\Sigma_u^+$, 23.58 eV	1IM, 10.25 eV	-4.46646 eV
2ID, 29.36 eV	$C^2\Sigma_u^+$ v = 3, 24.33 eV	1IM, 10.25 eV	-5.21556 eV
2ID, 29.36 eV	$X^2\Sigma_g^+$, 15.58 eV	3IM, 12.27 eV	1.516065 eV
2ID, 29.36 eV	$A^2\Pi_u$, 16.69 eV	3IM, 12.27 eV	0.403465 eV
2ID, 29.36 eV	$B^2\Sigma_u^+$, 18.75 eV	3IM, 12.27 eV	-1.65493 eV
2ID, 29.36 eV	$D^2\Pi_g$, 22.02 eV	3IM, 12.27 eV	-4.92393 eV
2ID, 29.36 eV	$C^2\Sigma_u^+$, 23.58 eV	3IM, 12.27 eV	-6.48693 eV
2ID, 29.36 eV	$C^2\Sigma_u^+$ v = 3, 24.33 eV	3IM, 12.27 eV	-7.23603 eV
4ID, 32.07 eV	**$X^2\Sigma_g^+$, 15.58 eV**	**3IM, 12.27 eV**	**4.225782 eV**
4ID, 32.07 eV	**$A^2\Pi_u$, 16.69 eV**	**3IM, 12.27 eV**	**3.113182 eV**
4ID, 32.07 eV	$B^2\Sigma_u^+$, 18.75 eV	3IM, 12.27 eV	1.054782 eV
4ID, 32.07 eV	$D^2\Pi_g$, 22.02 eV	3IM, 12.27 eV	-2.21422 eV
4ID, 32.07 eV	$C^2\Sigma_u^+$, 23.58 eV	3IM, 12.27 eV	-3.77722 eV
4ID, 32.07 eV	$C^2\Sigma_u^+$ v = 3, 24.33 eV	3IM, 12.27 eV	-4.52632 eV

Scattering diagrams

To emphasize the weaker features of the scattering, the scattering diagrams in the paper are plotted using a logarithmic intensity scale. Such a scale, of course, makes the scattering look more angularly dispersed. To illustrate this point the figure below (Figure SI1) shows the same data as Figure 2c but on a linear intensity scale. Comparison of these two figures allows the reader to appreciate the directionality of the scattering.

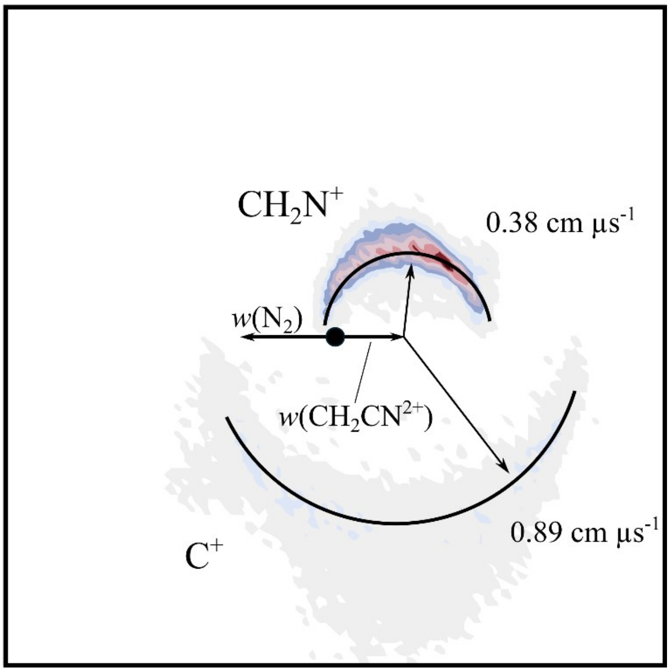
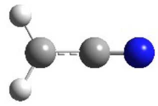
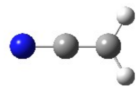
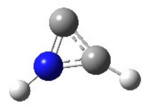
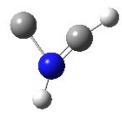
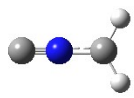
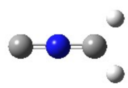
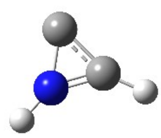
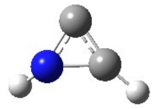
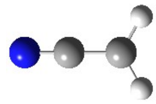
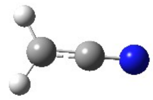
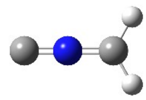
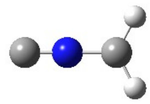


Figure SI1: CM scattering diagram for the reaction $CH_2CN^{2+} + N_2 \rightarrow CH_2N^+ + C^+ + N_2$ at a CM collision energy of 4.5 eV. The ion densities are represented with a linear scale, as opposed to a logarithmic scale (Figure 2c). The black dot indicates the position of the CM. See text for details.

Computed geometric minima.

Table SI2 Geometrical parameters for monocation and dication local minima discovered in computational investigation. See article text for details.

Structure	Label	Charge	*S*	Atom	x/ Å	y/Å	z/Å	Image
Linear	2LD	2	2	C	1.235753	-0.000005	-0.000004	
-CN Dication				C	-0.205149	0.000018	0.00004	
				N	-1.390202	-0.000007	-0.000021	
H2CCN_2				H	1.773876	-0.977257	-0.000036	
				H	1.773909	0.977229	-0.000036	
Linear	4LD	2	4	C	1.249836	0	0.000001	
-CN Dication				C	-0.107285	-0.000001	0.000023	
				N	-1.495421	0	-0.000012	
H2CCN_3				H	1.806321	-0.973619	-0.000032	
				H	1.80632	0.97362	-0.000032	
Cyclic	2CD	2	2		C	-0.145115	0.885056	
Dication					C	0.760323	-0.180413	
					N	-0.576016	-0.350058	
H2CCN_20					H	-1.379179	-1.045251	
					H	1.72004	-0.732201	
Cyclic	4CD	2	4		C	-0.936668	0.621212	
Dication					C	0.792369	0.233863	
					N	-0.070118	-0.621118	
H2CCN_21					H	-0.360456	-1.645383	
					H	1.717078	0.862763	
Isocyanate dication	2ID	2	2	C	1.115307	0	-1E-06	
H2CNC_1				N	-0.23876	0	0.000003	
				C	-1.37763	0	-2E-06	
				H	1.622619	0.978341	-1E-06	
				H	1.62262	-0.97834	-1E-06	
Isocyanate dication	4ID	2	4	C	1.045869	0.000058	0.000033	
H2CNC_2				N	-0.172331	-0.000279	-0.000145	
				C	-1.426037	0.000138	0.000095	
				H	1.743187	0.934037	0.000124	
				H	1.744137	-0.933255	0.000124	
Cyclic cation	1CM	1	1	C	-0.276799	0.930989	0	
H2CCN_24				C	0.74777	-0.107452	0.000001	
				N	-0.484985	-0.454413	0	
				H	-1.170414	-1.219172	-0.000001	
				H	1.739486	-0.541162	-0.000002	

Cyclic cation	3CM	1	3	C	0.020104	0.856409	-0.037304	
				C	0.763074	-0.239332	-0.009235	
H2CCN_25				N	-0.701098	-0.28557	0.113728	
				H	-1.382776	-0.773954	-0.479948	
				H	1.591395	-0.929518	-0.036909	
Linear cation	1LM	1	1	C	1.196732	0	-0.000003	
				C	-0.186113	0	0.000007	
H2CCN_4				N	-1.363094	0	-0.000003	
				H	1.738972	-0.94476	-0.000002	
				H	1.738972	0.94476	-0.000002	
Linear cation	3LM	1	3	C	0.000007	-1.18068	0	
				C	0	0.147922	0	
H2CCN_5				N	-0.000009	1.377495	0	
				H	0.00001	-1.722957	-0.947841	
				H	0.00001	-1.722957	0.947841	
Isocyanate	1IM	1	1	C	1.094949	0	0	
cation				N	-0.191289	0	-0.000001	
H2CNC_8				C	-1.412716	0	0.000001	
				H	1.622812	0.952004	0.000001	
				H	1.622811	-0.952005	0.000001	
Isocyanate	1IM	1	3	C	1.095245	0	0.000049	
cation				N	-0.224631	0	-0.000043	
H2CNC_9				C	-1.363954	0	0.000022	
				H	1.592335	0.956485	-0.000066	
				H	1.592336	-0.956485	-0.000066	

Scattering diagrams for the CID channel forming $HC_2N^+ + H^+$

The scattering diagrams below relate to the discussion in section 3.2 of the paper

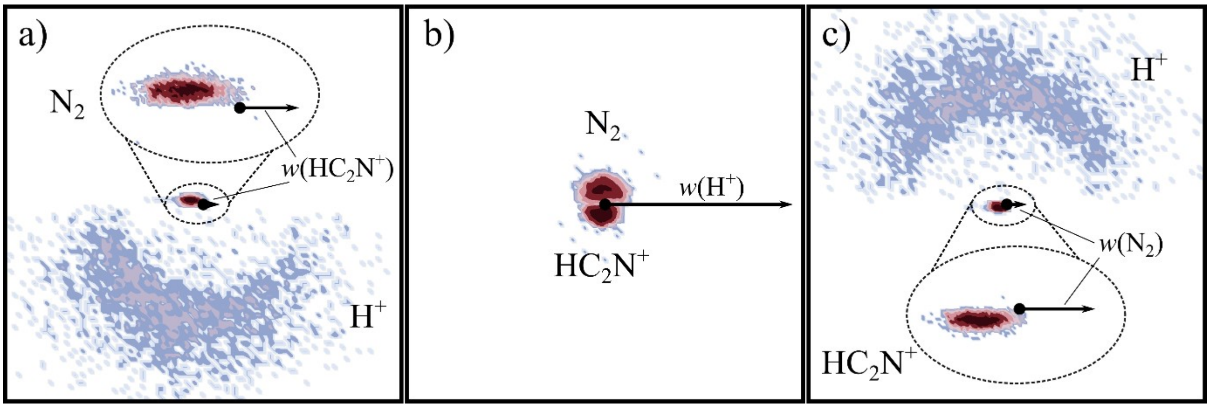


Figure SI2: IF scattering diagrams for the channel $CH_2CN^{2+} + N_2 \rightarrow HC_2N^+ + H^+ + N_2$ at a CM collision energy of 4.5 eV. a) The scattering of the H^+ and N_2 product fragments relative to the velocity of HC_2N^+. b) The scattering of the N_2 and HC_2N^+ fragments relative to H^+. c) The scattering of H^+ and HC_2N^+ relative to N_2.

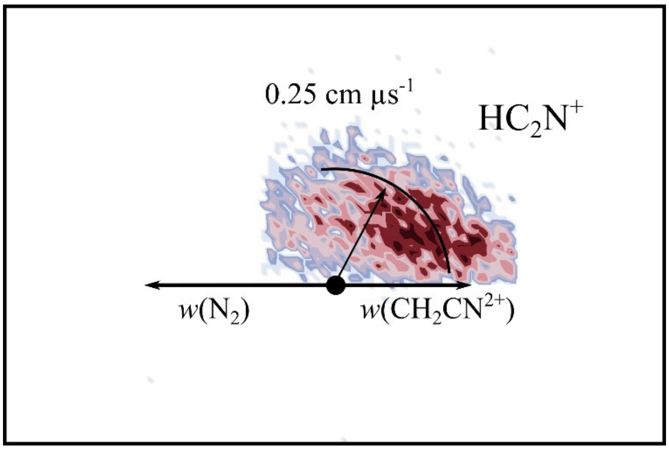


Figure SI3: CM scattering of the HC_2N^+ product for the channel $CH_2CN^{2+} + N_2 \rightarrow HC_2N^+ + H^+ + N_2$ at a CM collision energy of 4.5 eV.

References for SI

1 A. Kramida, Y. Ralchenko, J. Reader and NIST ASD Team, Eds., *NIST Atomic Spectra Database (version 5.6.1)*, National Institute of Standards and Technology, Gaithersburg, MD, 2020.

2 W. C. Martin, R. Zalubas and A. Musgrove, *J. Phys. Chem. Ref. Data*, 1990, **19**, 821–880.