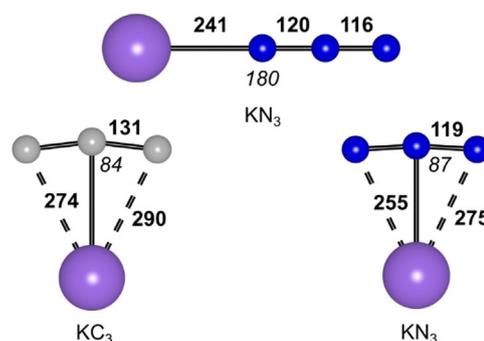


## Matrix-Isolation Spectroscopy

## IR-Laser Ablation of Potassium Cyanide: A Surprisingly Simple Route to Polynitrogen and Polycarbon Species

Frenio A. Redeker, Helmut Beckers, and Sebastian Riedel\*<sup>[a]</sup>

**Abstract:** Pulsed laser irradiation of solid potassium cyanide (KCN) produces, besides free nitrogen and carbon atoms, the molecular species KN and KC which are potential candidates for interstellar species of potassium. Additionally,  $N_3$ ,  $N_3^-$ ,  $KN_3$ ,  $C_3$ ,  $C_3^-$ , and  $KC_3$  are produced and isolated in solid noble gases as well as in solid  $N_2$ . Molecular potassium nitrene (KN) reacts with dinitrogen in neon and argon matrices after photochemical excitation ( $\lambda = 470$  nm) forming molecular end-on ( $C_{\infty v}$ ) and side-on ( $C_{2v}$ ) potassium azide isomers. The side-on isomer ( $C_{2v}$ ) is thermodynamically favored at the CCSD(T)/ma-def2-TZVP level of theory. It can be obtained from the end-on isomer by UV-irradiation ( $\lambda = 273$  nm).



**Figure 1.** Structures of the  $KC_3$ , end-on  $KN_3$ , and side-on  $KN_3$  ion pairs computed at the CCSD(T)/ma-def2-TZVP level of theory. Bold and italic numbers indicate bond lengths [pm] and bond angles [°], respectively.

Potassium cyanide is one of the metal cyanide species detected in proximity to a star in space<sup>[1]</sup> and KC, KN, and KO are supposed to be potential candidates for further interstellar species of potassium.<sup>[2]</sup> While KC and KO were characterized by their rotational spectra,<sup>[3]</sup> to our knowledge no spectroscopic gas-phase study has yet been published for KN. However, potassium nitrene has been predicted to be stable with a bond dissociation energy of 81 kJ mol<sup>-1</sup> at the MRCI(+Q)/triple- $\zeta$  level of theory.<sup>[2]</sup>

Pulsed IR-laser ablation of solid salts was recently shown to be a particularly suitable method to produce and characterize anionic complexes. Recent examples are the homoatomic anions  $Cl_3^-$  and  $F_3^-$ , which were produced by co-deposition of IR-laser ablated potassium halide,  $KX$  ( $X = Cl$  and  $F$ , respectively), with gaseous  $X_2$ /noble gas mixtures at cryogenic temperatures.<sup>[4]</sup> Two further homoatomic anions, which are of particular interest for the present work, are the  $C_3^-$  and  $N_3^-$  anions. The first one was assigned by Szczepanski et al. to a band at 1721.8 cm<sup>-1</sup> after isolation and electron bombardment of laser ablated graphite in a solid argon matrix.<sup>[5]</sup> The free  $N_3^-$  anion

was associated with an IR band at 2003.5 cm<sup>-1</sup> by Michl and co-workers, which was observed in pure  $N_2$  matrices after atom/ion bombardment.<sup>[6]</sup> It was later also detected by Andrews and co-workers after co-deposition of laser ablated Ga, In, and Tl atoms in solid nitrogen,<sup>[7]</sup> and in argon matrices, where this band appeared at 1991.9 cm<sup>-1</sup>.<sup>[8]</sup>

As a logical extension of our former work<sup>[4]</sup> we present in this study results obtained by laser ablation of the ternary system potassium cyanide (KCN). Matrix-isolation IR-spectra of thermally evaporated sodium and potassium cyanide were reported previously by Ismail, Hauge, and Margrave (IHM).<sup>[9]</sup> The IR spectra obtained by us from IR-laser ablation of potassium cyanide deposited in solid argon are in the spectral region above 2000 cm<sup>-1</sup> are very similar to those described by IHM. We find KNCO and CO as the main impurities in our spectra due to the high temperature reaction of KCN with  $CO_2$  formed by laser ablation of  $CO_3^-$  impurities. The CN stretching region of the IR spectra of laser ablated KCN isolated in neon and argon is shown in Figures S1 and S2 in the Supporting Information. Based on the work by IHM, the observed bands at 2048.7, 2059.3/2061.3, and 2079.6 cm<sup>-1</sup> in argon and 2047.0, 2061.2, and 2075.7 cm<sup>-1</sup> in neon are assigned to monomeric, oligomeric, and polymeric potassium cyanide, respectively. In contrast to the thermal evaporation, which essentially results in isolated monomeric and oligomeric ion pairs, laser ablation allows for the preparation of free anions, for example, laser ablation of alkali halides ( $MX$ ,  $X = Cl, F$ ) allowed us to study not only isolated  $MX$  ion pairs in solid noble gas matrices, but also to isolate free anions such as the free  $X_3^-$  ions in the presence of  $X_2$ .<sup>[4]</sup> It was, therefore, rather surprising to find that laser ablation of KCN does not produce free  $CN^-$  ions, which have a

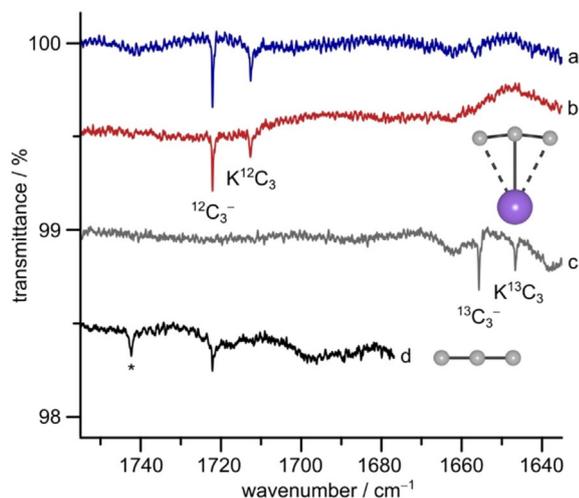
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reported band at  $2053.1\text{ cm}^{-1}$  in solid neon<sup>[10]</sup> (cf. Figure S1, Supporting Information).

In IR spectra obtained from laser ablated potassium cyanide trapped in solid argon at 12 K we found two new bands in a region at  $1722.0$  and  $1712.5\text{ cm}^{-1}$  where we do not expect any CN stretching bands (Figure 2). Both bands reveal a large  $^{13}\text{C}$



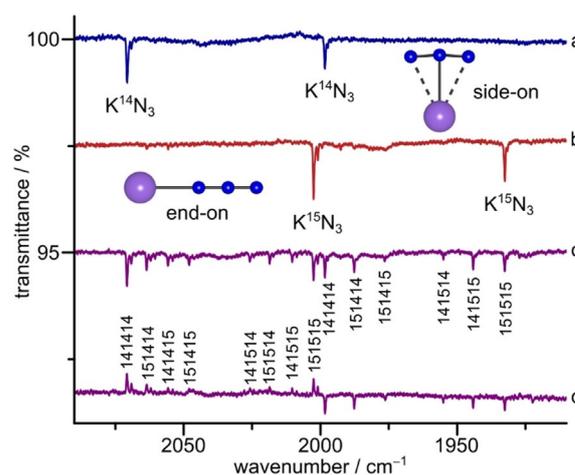
**Figure 2.** IR spectra recorded after deposition of laser ablated a)  $\text{K}^{12}\text{C}^{14}\text{N}$ , b)  $\text{K}^{12}\text{C}^{15}\text{N}$ , c)  $\text{K}^{13}\text{C}^{14}\text{N}$ , and d)  $\text{Na}^{12}\text{C}^{14}\text{N}$  in excess argon at 12 K. \* Unknown species.

shift of  $-66\text{ cm}^{-1}$  in experiments using  $\text{K}^{13}\text{CN}$ , and when KCN was replaced by NaCN it became evident that the  $1722.0\text{ cm}^{-1}$  band is metal independent, whereas the  $1712.5\text{ cm}^{-1}$  band is not. The metal-independent band is close to the band at  $1721.8\text{ cm}^{-1}$  previously assigned by Szczepanski et al. to the antisymmetric stretch ( $\nu_3$ ) of the linear  $\text{C}_3^-$  anion.<sup>[5]</sup> Here we confirm the assignment of this band based on its metal independency and its  $^{12/13}\text{C}$  isotope pattern obtained after pulsed laser deposition of a 1:1 mixture of  $\text{K}^{12}\text{CN}$  and  $\text{K}^{13}\text{CN}$  in argon (Figure S6, Supporting information). The 1:1 isotopic mixture yielded six  $^{12/13}\text{C}_3^-$  isotopologues. The band positions of all  $\text{C}_3^-$  isotopologues are displayed in Table 1.

The metal-dependent band at  $1712.5\text{ cm}^{-1}$  in Figure 2 has almost the same  $^{13}\text{C}$  isotopic shift as the free  $\text{C}_3^-$  anion. It is assigned to the  $\nu_3$  stretch of the corresponding ion pair  $\text{KC}_3$  ( $\text{C}_{2v}$ ) which has been predicted to be the most stable potassium doped carbon cluster  $\text{KC}_n$  ( $n = 1-10$ ) by a recent DFT study.<sup>[11]</sup>

Our quantum-chemical calculations at the CCSD(T)/ma-def2-TZVP level also support this assignment (Table 1, Figure 1). The full isotope pattern of  $\text{KC}_3$  is not as nicely resolved as for  $\text{C}_3^-$  due to lower yields (Figure S6, Supporting Information), so that only three of its isotopologues can be confidently assigned. The band at  $1742.3\text{ cm}^{-1}$  observed after laser ablation of natural NaCN (Figure 2d) immediately suggests an assignment to  $\text{NaC}_3$  since the  $\nu_3(\text{C}_3^-)$  stretch of  $\text{MC}_3$  is intuitively expected to shift to higher wavenumbers for lighter alkali metals. However, CCSD(T) calculations predict the  $\nu_3(\text{C}_3^-)$  of  $\text{NaC}_3$   $16\text{ cm}^{-1}$  lower than for  $\text{KC}_3$ . Therefore, this band must yet remain unassigned.

Upon irradiation of the neon matrices at 6 K with blue LED-light ( $\lambda = 470\text{ nm}$ ) two new bands at  $2070.8$  and  $1998.4\text{ cm}^{-1}$  appeared (Figure 3a). Subsequent irradiation with a  $\lambda = 273\text{ nm}$  led to conversion of the  $2070.8\text{ cm}^{-1}$  into the  $1998.4\text{ cm}^{-1}$  band, indicating that the two bands correspond to two different molecular species. In solid argon at 12 K these bands shifted to  $2057.0$  and  $1988.9\text{ cm}^{-1}$  (Table 2) and their intensity increased by addition of small amounts of  $\text{N}_2$  to the matrix gas. While no  $^{12/13}\text{C}$  isotope shifts were observed in the experiments performed with  $\text{K}^{13}\text{CN}$ , both bands revealed large



**Figure 3.** IR spectra recorded after co-deposition of laser ablated KCN with  $\text{N}_2$  in solid Ne at 6 K. Difference spectra a) after deposition of  $\text{K}^{12}\text{C}^{14}\text{N}$  with  $^{14}\text{N}_2$  (0.5%) in Ne and photolysis ( $\lambda = 470\text{ nm}$ ), b) after deposition of  $\text{K}^{12}\text{C}^{15}\text{N}$  with  $^{15}\text{N}_2$  (0.5%) in Ne and photolysis ( $\lambda = 470\text{ nm}$ ), c) after deposition of  $\text{K}^{12}\text{C}^{14}\text{N}/\text{K}^{12}\text{C}^{15}\text{N}$  (1:1) with  $^{14}\text{N}_2/^{15}\text{N}_2$  (1:1, 0.2%) in Ne and photolysis with  $\lambda = 470$  and d) after photolysis of c) with  $\lambda = 273\text{ nm}$ . Bands pointing upwards indicate depletion and bands pointing downwards formation of the corresponding species.

Species	121212	131212	131213	121312	131312	131313
$\text{C}_3^-$ (this work) <sup>[b]</sup>	1722.0	1711.5 (−10.5)	1700.2 (−21.8)	1678.1 (−43.9)	1667.3 (−54.7)	1655.6 (−66.4)
$\text{C}_3^-$ (Ref. [5b]) <sup>[b]</sup>	1721.8	1711.2 (−10.6)	1699.9 (−21.9)	1677.7 (−44.1)	1667.1 (−54.7)	1655.5 (−66.3)
$\text{KC}_3$ (this work) <sup>[b]</sup>	1712.5	1701.9 (−10.6)	1691.1 <sup>[d]</sup> (−21.4)	1668.8 <sup>[d]</sup> (−43.7)	1657.2 <sup>[d]</sup> (−55.3)	1646.5 (−66.0)
$\text{KC}_3$ (this work) <sup>[c]</sup>	1727.1	1716.4 (−10.7)	1704.8 (−22.3)	1682.3 (−44.8)	1671.3 (−55.8)	1659.4 (−67.7)

[a] Isotopic shifts with respect to the main isotopologue are given in parentheses. The isotopologues of  $\text{C}_3^-$  are abbreviated by the masses of their carbon isotopes: 131212 is equivalent to  $\text{K}^{13}\text{C}^{12}\text{C}^{12}\text{C}$ . Note that 131212 and 121313 are equivalent to 121213 and 131312, respectively. [b] Solid argon. [c] Calculated harmonic wavenumbers (CCSD(T)/ma-def2-TZVP). [d] Tentatively assigned band with low intensity (Figure S6, Supporting Information).

**Table 2.** Band positions [ $\text{cm}^{-1}$ ] of IR active  $\text{N}_3$  stretches of the end-on ( $C_{\infty v}$ ) and side-on ( $C_{2v}$ ) potassium azide isotopologues.<sup>[a]</sup>

$C_{\infty v}$	141414	151414	141415	151415	141514	151514	141515	151515
$\nu_3$ (calcd) <sup>[b]</sup>	2124.5	2116.7 (−7.8)	2108.7 (−15.8)	2100.3 (−24.2)	2077.1 (−47.4)	2069.3 (−55.2)	2060.9 (−63.6)	2052.4 (−72.1)
$\nu_3$ (solid Ne)	2070.8	2063.6 (−7.2)	2055.8 (−15.0)	2048.0 (−22.8)	2025.8 (−45.0)	2018.6 (−52.2)	2010.3 (−60.5)	2002.5 (−68.3)
$\nu_3$ (solid Ar)	2057.0	2049.3 (−7.7)	n.o.	n.o.	n.o.	n.o.	n.o.	1989.2 (−67.8)
$\nu_3$ (solid $\text{N}_2$ )	2048.5	2039.9 (−8.6)	2035.0 (−13.5)	2026.2 (−22.3)	2003.4 (−45.1)	1995.1 (−53.4)	1989.9(−58.6)	1980.9 (−67.6)
$\nu_1$ (calcd) <sup>[b]</sup>	1357.5	1330.9 (−26.6)	1338.0 (−19.5)	1311.7 (−45.8)	1357.3 (−0.2)	1330.5 (−27.0)	1337.9 (−19.6)	1311.5 (−46.0)
$\nu_1$ (solid Ne)	1344.6	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	1299.6 (−45.0)
$C_{2v}$	141414	151414	151415	141514	151514	151515		
$\nu_3$ (calcd) <sup>[b]</sup>	2038.8	2027.5 (−11.3)	2015.7 (−23.1)	1993.4 (−45.4)	1981.8 (−57.0)	1969.7 (−69.1)		
$\nu_3$ (solid Ne)	1998.4	1987.6 (−10.8)	1976.5 (−21.9)	1955.1 (−43.3)	1944.2 (−54.2)	1932.6 (−65.8)		
$\nu_3$ (solid Ar)	1988.9	1978.3 (−10.6)	n.o.	1945.9 (−43.0)	1935.2 (−53.7)	1923.5 (−65.4)		
$\nu_3$ (solid $\text{N}_2$ )	2006.5	1996.1 (−10.4)	1984.5 (−22.0)	1962.9 (−43.6)	1951.6 (−54.9)	1940.5 (−66.0)		

[a] Isotopic shifts with respect to the main isotopologue are given in parentheses. The isotopologues of  $\text{N}_3^-$  are abbreviated by the masses of their nitrogen isotopes: 151414 is equivalent to  $\text{K}^{15}\text{N}^{14}\text{N}^{14}\text{N}$ . In case of the linear isomer the potassium ion is sitting to the left of the number series. In case of the T-shaped isomer 151414 and 141515 are equivalent to 141415 and 151514, respectively. Bands that were too weak for a clear assignment are indicated with n.o. (not observed). [b] Calculated harmonic wavenumbers (CCSD(T)/ma-def2-TZVP).

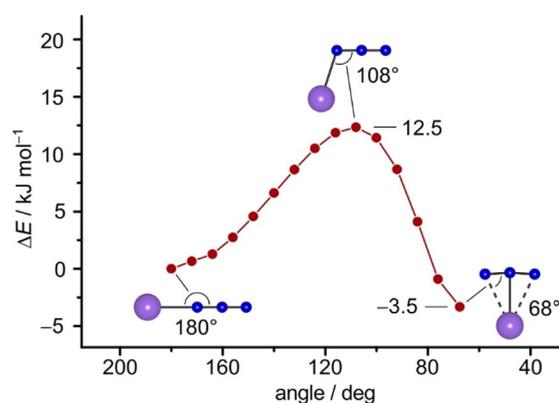
$^{14/15}\text{N}$  isotope shifts of  $-68.3$  ( $2070.8 \text{ cm}^{-1}$ ) and  $-65.8 \text{ cm}^{-1}$  ( $1998.4 \text{ cm}^{-1}$ ), respectively, in experiments using  $^{15}\text{N}$  isotopically enriched  $\text{KC}^{15}\text{N}$  and  $^{15}\text{N}_2$  doped neon (Figure 3 b). These large isotope shifts are strong evidence that only nitrogen atoms are involved in the corresponding vibrational modes.

In experiments using a mixture of  $\text{K}^{14}\text{N}/\text{K}^{15}\text{N}$  (1:1) as well as neon gas doped with a 1:1  $^{14}\text{N}_2/^{15}\text{N}_2$  mixture (Figure 3 c), the higher band split into eight and the lower into six bands. In analogy with  $\text{C}_3^-$  and  $\text{KC}_3$ , a pattern of six isotopologues would be expected for the free  $\text{N}_3^-$  anion or side-on  $\text{KN}_3$  ( $C_{2v}$  Figure 1). The pattern of eight bands is indicative of three chemically inequivalent nitrogen atoms as in molecular end-on  $\text{KNNN}$  ( $C_{\infty v}$  Figure 1). Thus the higher-frequency band at  $2070.8 \text{ cm}^{-1}$  is assigned to the  $\nu_3(\text{N}_3^-)$  stretch of molecular end-on  $\text{KN}_3$  which is in good agreement with the calculated band position ( $2124.5 \text{ cm}^{-1}$ , CCSD(T)/ma-def2-TZVP), as well as with the predicted  $^{14/15}\text{N}$  isotopic shifts (Table 2). The lower-frequency band at  $1998.4 \text{ cm}^{-1}$  is in good agreement with the computed  $\nu_3$  band position of side-on  $\text{KN}_3$  ( $2038.8 \text{ cm}^{-1}$ , CCSD(T)/ma-def2-TZVP) and close to the reported  $\nu_3$  stretch of the free  $\text{N}_3^-$  anion in solid nitrogen at  $2003.5 \text{ cm}^{-1}$ .<sup>[6a,7]</sup> The conversion of end-on  $\text{KN}_3$  into the carrier of the  $1998.4 \text{ cm}^{-1}$  band during UV irradiation ( $\lambda = 273 \text{ nm}$ , Figure 3 d) supports its assignment to side-on  $\text{KN}_3$  rather than to free  $\text{N}_3^-$ . The symmetric stretch of side-on  $\text{KN}_3$  ( $\nu_1$ ) has almost no IR intensity and, therefore, could not be observed in our experiments, while the corresponding mode of end-on  $\text{KN}_3$  has some IR intensity and could be observed for end-on  $\text{K}^{14}\text{N}_3$  and  $\text{K}^{15}\text{N}_3$  in solid neon (Table 2, Figure S9, Supporting Information).

In solid nitrogen matrices no irradiation was needed to produce  $\text{KN}_3$ . After deposition the  $^{14}\text{N}$  spectra showed a strong band at  $2048.5$  with a site at  $2049.3 \text{ cm}^{-1}$  for end-on  $\text{K}^{14}\text{N}_3$  and the broad band of free  $^{14}\text{N}_3^-$  as described by Michl and Andrews at  $2003.5$  with a site at  $2005.6 \text{ cm}^{-1}$ . Upon annealing to  $25 \text{ K}$  the band at  $2048.5 \text{ cm}^{-1}$  increased drastically while the  $\text{N}_3^-$  band decreased so that another band at  $2006.5 \text{ cm}^{-1}$  became visible. The  $2006.5 \text{ cm}^{-1}$  band has not been described by Michl or Andrews and is assigned to the antisymmetric

azide stretch ( $\nu_3$ ) of side-on  $\text{KN}_3$  in solid nitrogen. In the mixed isotope experiment where laser ablated  $\text{K}^{14}\text{N}/\text{K}^{15}\text{N}$  (1:1) was co-deposited with pure  $^{14}\text{N}_2/^{15}\text{N}_2$  (1:1) at  $12 \text{ K}$  (Figure S7, Supporting Information), the band at  $2048.5 \text{ cm}^{-1}$  split into an octet, whereas the band at  $2006.5 \text{ cm}^{-1}$  split into a sextet, as expected for end-on and side-on  $\text{KN}_3$  (Figure S7b, Supporting Information). Upon irradiation with UV light ( $\lambda = 273 \text{ nm}$ ) the free  $\text{N}_3^-$  band was depleted, while the  $2048.5$  and  $2006.5 \text{ cm}^{-1}$  bands were not (Figure S7c, Supporting Information). All calculated and observed experimental band positions of the anti-symmetric  $\text{N}_3^-$ -stretches of side-on and end-on  $\text{KN}_3$  in Ne, Ar, and  $\text{N}_2$  are displayed in Table 2.

Calculations at the CCSD(T)/ma-def2-TZVP level of theory predict that side-on  $\text{KN}_3$  is  $3.5 \text{ kJ mol}^{-1}$  lower in energy than end-on  $\text{KN}_3$ . The barrier for the rearrangement from end-on to side-on obtained from a relaxed surface scan along the K–N–N bond angle (Figure 4) is predicted to be  $12.5 \text{ kJ mol}^{-1}$  which appears to be high enough that the rearrangement could not be observed by annealing in any experiments. In neon, however, there seems to be a photochemical equilibrium between the end-on and the side-on form: Immediately after formation of the two isomers by irradiation with blue light ( $\lambda = 470 \text{ nm}$ )



**Figure 4.** Relaxed surface scan of the potassium azide bond angle at the CCSD(T)/ma-def2-TZVP level of theory.

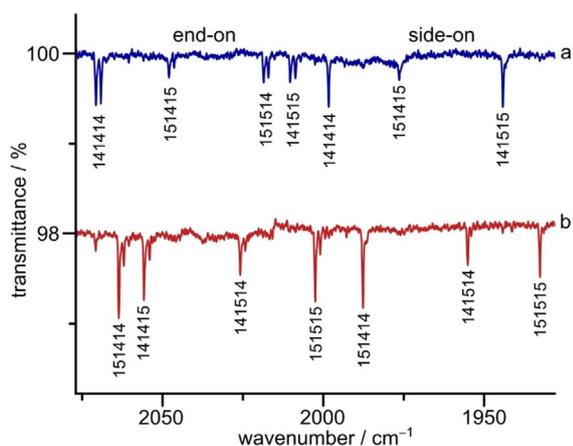
the ratio end-on/side-on was about 3/2 whereas after irradiation with UV light ( $\lambda = 273$  nm) it changed to 2/3. While this interconversion was only observed in neon, in argon, the side-on  $\text{KN}_3$  is the main product after  $\lambda = 470$  nm photolysis.

In principle, three reaction mechanisms can be considered for the formation of molecular  $\text{KN}_3$  in the experiments described above: i) recombination of  $\text{K}^+$  and  $\text{N}_3^-$  ions, ii) reaction of potassium atoms and  $\text{N}_3$  radicals, and iii) reaction of potassium nitrene (KN) and  $\text{N}_2$  molecules [Eq. (1)]. In the neon and argon experiments, however, the former two reactions can be ruled out since neither  $\text{N}_3^-$  anions nor  $\text{N}_3$  radicals were observed in these matrices. KN is calculated to have a triplet ground state ( $\text{MRCI}(+\text{Q})$ ),<sup>[2]</sup> while the reaction of  $\text{KN} + \text{N}_2$  (1) is assumed to proceed with excited singlet KN molecules after photoexcitation and intersystem crossing (ISC) to their lowest singlet state. Note that we have not observed the vibrational band of KN ( $324.4 \text{ cm}^{-1}$ )<sup>[2]</sup> in our experiments, because this band is expected to be rather weak and beyond the range of our MCT detector. Nevertheless, KN should be present as a key intermediate for the formation of  $\text{KN}_3$ .



In solid nitrogen, large amounts of end-on  $\text{KN}_3$  and only small amounts of side-on  $\text{KN}_3$  were observed after annealing to 25 K. At the same time high amounts of free  $\text{N}_3^-$  were consumed during this process, suggesting that  $\text{KN}_3$  might also be formed by a recombination of  $\text{K}^+$  and  $\text{N}_3^-$  ions in solid nitrogen. This observation explains the high abundance of end-on compared to side-on  $\text{KN}_3$  in solid nitrogen: The partial negative charges on the two terminal nitrogen atoms in  $\text{N}_3^-$  favor an electrostatic recombination of  $\text{K}^+$  and  $\text{N}_3^-$  and the formation of the thermodynamically less stable end-on  $\text{KN}_3$ .

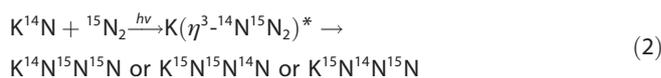
Figure 5 shows the  $^{14/15}\text{N}$  isotopic IR band patterns obtained after co-deposition of laser ablated  $\text{KC}^{14}\text{N}$  with  $^{15}\text{N}_2$  doped neon (a) and of  $\text{KC}^{15}\text{N}$  with  $^{14}\text{N}_2$  doped neon (b) after irradiation with blue light ( $\lambda = 470$  nm). Obviously, spectra Figure 5a and



**Figure 5.** IR spectra recorded after co-deposition of laser ablated KCN with  $\text{N}_2$  in solid Ne at 6 K. Difference spectra after photolysis ( $\lambda = 470$  nm, 10 min) of a)  $\text{K}^{12}\text{C}^{14}\text{N}$  with  $^{15}\text{N}_2$  (0.2%), b)  $\text{K}^{12}\text{C}^{15}\text{N}$  with traces of  $^{14}\text{N}_2$ . Bands pointing downwards indicate formation of the corresponding species.

b are complementary. Due to the purity of 98 atom %  $^{15}\text{N}$  of the  $\text{KC}^{15}\text{N}$  used for the experiment, traces of the  $\text{K}^{14}\text{N}^{14}\text{N}^{14}\text{N}$  isotopologue can be observed in Figure 5b. The high yield of  $\text{K}^{15}\text{N}_3$  in Figure 5b indicates that  $^{15}\text{N}_2$  is formed in substantial amounts by recombination of  $^{15}\text{N}$  atoms from laser ablated  $\text{KC}^{15}\text{N}$ . The absence of any ( $^{15}\text{N}_2^{14}\text{N}$ ) isotopologues in Figure 5b and of ( $^{14}\text{N}_2^{15}\text{N}$ ), and  $\text{K}^{15}\text{N}^{15}\text{N}^{15}\text{N}$  isotopologues in Figure 5a implies the absence of a reaction between  $\text{K}^{15}\text{N}$  and  $^{14}\text{N}_2$  producing  $\text{K}^{14}\text{N}$  and  $^{14}\text{N}^{15}\text{N}$  or vice versa. On the other hand,  $\text{K}^{14}\text{N}$  can react with  $^{15}\text{N}_2$  not only to form the addition product  $\text{K}^{14}\text{N}^{15}\text{N}^{15}\text{N}$  but also to form  $\text{K}^{15}\text{N}^{14}\text{N}^{15}\text{N}$  and  $\text{K}^{15}\text{N}^{15}\text{N}^{14}\text{N}$ . This observation may indicate a  $\text{K}(\eta^3\text{-N}_3)$  ion-pair-intermediate or transition state involving a cyclic  $\eta^3\text{-N}_3^-$  ring in the course of the photoinduced reaction that finally rearranges to one of the three possible mixed isotopologues according to Equation (2). Such a transient cyclic  $\text{N}_3^-$  has already been postulated by Michl and co-workers.<sup>[6b]</sup>

In addition to the free  $\text{C}_3^-$  and  $\text{N}_3^-$  anions and the ion pairs  $\text{KC}_3$  and  $\text{KN}_3$  the IR spectra of the deposits obtained from IR laser ablation of potassium cyanide also showed bands which can be attributed to well-known free radicals such as the  $\text{C}_3$ ,<sup>[12]</sup>  $\text{N}_3$ ,<sup>[6a]</sup>  $\text{CN}$ ,<sup>[10]</sup>  $\text{NCN}$ ,<sup>[13]</sup> and  $\text{CNN}$ <sup>[14]</sup> radicals (for further details and a discussion of the reaction mechanisms see the Supporting Information).



In the present paper we have shown that IR laser ablation of potassium cyanide leads to a complex mixture of polynitrogen and polycarbon species. In this study, molecular  $\text{KN}_3$  and  $\text{KC}_3$  are reported for the first time. To the best of our knowledge, previous IR spectroscopic studies on potassium azide were performed only on crystalline  $\text{KN}_3$ ,<sup>[15]</sup> while several studies were reported on molecular group 2,<sup>[16]</sup> group 13,<sup>[7,8]</sup> and transition-metal azides.<sup>[17]</sup> The ion pair  $\text{KN}_3$  exists in an end-on and a side-on form, which are separated by a barrier of about  $12 \text{ kJ mol}^{-1}$  at coupled-cluster level. Molecular potassium nitrene (KN) is assumed to be a key intermediate produced by IR-laser ablation of potassium cyanide (KCN), that reacts photochemically with dinitrogen to molecular potassium azide ( $\text{KN}_3$ ). Laser ablation of KCN could therefore be a suitable route for the gas-phase generation and spectroscopic detection of the elusive KN molecule, which is of interest as a potential interstellar molecule. Awareness of the photochemical reaction of KN and  $\text{N}_2$  might also enable a better understanding of mechanisms involved in processes of photochemical nitrogen fixation.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** laser ablation · matrix-isolation spectroscopy · polycarbon compounds · polynitrogen compounds · quantum-chemical calculations

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