Matrix-Isolation Spectroscopy

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

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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$_4^-$, KN$_2^-$, C$_2^-$, 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$_{endo}$) and side-on (C$_{side}$) potassium azide isomers. The side-on isomer (C$_{side}$) 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).

Potassium cyanide is one of the metal cyanide species detected in proximity to a star in space and KN, KO, and KC are supposed to be potential candidates for further interstellar species of potassium. While KC and KO were characterized by their rotational spectra, 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 dissociation energy of 81 kJ mol$^{-1}$ at the MRCI(+Q)/triple-$\zeta$ level of theory. 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 homonuclear 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. Two further homonuclear 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$^{-1}$ after isolation and electron bombardment of laser ablated graphite in a solid argon matrix. The free N$_3^-$ anion was associated with an IR band at 2003.5 cm$^{-1}$ by Michl and co-workers, which was observed in pure N$_2$ matrices after atom/ion bombardment. It was later also detected by Andrews and co-workers after co-deposition of laser ablated Ga, In, and TI atoms in solid nitrogen and in argon matrices, where this band appeared at 1991.9 cm$^{-1}$.

As a logical extension of our former work, 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). 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$^{-1}$ 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$^{-1}$ in argon and 2047.0, 2061.2, and 2075.7 cm$^{-1}$ 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$_2$.[6] It was, therefore, rather surprising to find that laser ablation of KCN does not produce free CN$^-$ ions, which have a...
reported band at 2053.1 cm⁻¹ in solid neon[10] (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 cm⁻¹ where we do not expect any CN stretching bands (Figure 2). Both bands reveal a large ¹³C shift of −66 cm⁻¹ in experiments using K¹³CN, and when KCN was replaced by NaCN it became evident that the 1722.0 cm⁻¹ band is metal independent, whereas the 1712.5 cm⁻¹ band is not. The metal-independent band is close to the band at 1721.8 cm⁻¹ previously assigned by Szczepanski et al. to the antisymmetric stretch (ν₃) of the linear C₃⁻ anion.[13] Here we confirm the assignment of this band based on its metal independence and its ¹²/¹³C isotope pattern obtained after pulsed laser deposition of a 1:1 mixture of K¹³CN and K¹²CN in argon (Figure S6, Supporting information). The 1:1 isotopic mixture yielded six ¹²/¹³C isotope patterns. The band positions of all C₃⁻ isotopologues are displayed in Table 1.

The metal-dependent band at 1712.5 cm⁻¹ in Figure 2 has almost the same ¹³C isotope shift as the free C₃⁻ anion. It is assigned to the ν₁ stretch of the corresponding ion pair KC₃ (C₃⁺) which has been predicted to be the most stable potassium doped carbon cluster KC₃ (n = 1–10) by a recent DFT study.[11]

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 KC₃ is not as nicely resolved as for C₃⁻ due to lower yields (Figure S6, Supporting information), so that only three of its isotopologues can be confidently assigned. The band at 1742.3 cm⁻¹ observed after laser ablation of natural NaCN (Figure 2d) immediately suggests an assignment to NaC₃, since the υ₁(C₃⁻) stretch of MnC₃ is intuitively expected to shift to higher wavenumbers for lighter alkali metals. However, CCSD(T) calculations predict the υ₁(C₃⁻) of NaC₃ 16 cm⁻¹ lower than for KC₃. Therefore, this band must yet remain unassigned.

Upon irradiation of the neon matrices at 6 K with blue LED-light (λ = 470 nm) two new bands at 2070.8 and 1998.4 cm⁻¹ appeared (Figure 3a). Subsequent irradiation with a λ = 273 nm led to conversion of the 2070.8 cm⁻¹ into the 1998.4 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 cm⁻¹ (Table 2) and their intensity increased by addition of small amounts of N₂ to the matrix gas. While no ¹²/¹³C isotope shifts were observed in the experiments performed with K¹²CN, both bands revealed large

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**Table 1.** Band positions (cm⁻¹) of the antisymmetric C₃⁻ stretching vibration (υ₃) of the isotopologues of free C₃⁻ (D₃h) and T-shaped KC₃ (C₃⁺).[8]

| Species | 121212 | 121312 | 131213 | 121312 | 131312 | 131312 | 131312 | 131312 |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| C₃⁻ (this work)[8] | 1722.0 | 1711.5 (−10.5) | 1709.2 (−21.8) | 1671.1 (−43.9) | 1667.3 (−54.7) | 1655.6 (−66.4) | 1655.6 (−66.4) | 1655.6 (−66.4) |
| C₃⁻ (Ref. [5b] )[8] | 1721.8 | 1711.2 (−10.6) | 1699.9 (−21.9) | 1677.7 (−44.1) | 1667.1 (−54.7) | 1655.5 (−66.3) | 1655.5 (−66.3) | 1655.5 (−66.3) |
| KC₃ (this work)[8] | 1712.5 | 1701.9 (−10.6) | 1691.1[H] (−21.4) | 1668.8[470] (−43.7) | 1657.2[470] (−55.3) | 1646.5 (−66.0) | 1646.5 (−66.0) | 1646.5 (−66.0) |
| KC₃ (this work)[8] | 1727.1 | 1716.4 (−10.7) | 1704.8 (−22.3) | 1682.3 (−44.8) | 1671.3 (−55.8) | 1659.4 (−67.7) | 1659.4 (−67.7) | 1659.4 (−67.7) |

[a] Isotopic shifts with respect to the main isotopologue are given in parentheses. The isotopologues of C₃⁻ are abbreviated by the masses of their carbon isotopes: 131212 is equivalent to K¹²C¹²C¹²C. 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 [cm$^{-1}$] of IR active $N_2$ stretches of the end-on ($C_{ee}$) and side-on ($C_{ev}$) potassium azide isotopologues.$^{[a]}$

| $C_{ee}$ | 141414 | 151414 | 141415 | 151415 | 141514 | 151514 | 141515 | 151515 |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| $v_1$ (calcld$^{[h]}$) | 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) |
| $v_1$ (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) |
| $v_1$ (solid Ar) | 2057.0 | 2049.3 (−7.7) | n.o. | n.o. | n.o. | n.o. | n.o. | 1989.2 (−67.8) |
| $v_2$ (solid $N_2$) | 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) |
| $v_1$ (calcld$^{[c]}$) | 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) |
| $v_1$ (solid Ne) | 1344.6 | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | 1299.6 (−45.0) |

[a] Isotopic shifts with respect to the main isotopologue are given in parentheses. The isotopologues of $N_2^-$ are abbreviated by the masses of their nitrogen isotopes: $14\text{N}^2\text{N}^{-}$ is equivalent to $15\text{N}^2\text{N}^{-}$. 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 151515 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$\text{N}$ isotope shifts of −68.3 (2070.8 cm$^{-1}$) and −65.8 cm$^{-1}$ (1998.4 cm$^{-1}$), respectively, in experiments using 14$\text{N}$ isotopically enriched KC$^{14}$N and 14$\text{N}$I$^{15}$N doped neon (Figure 3b). These large isotopic shifts are strong evidence that only nitrogen atoms are involved in the corresponding vibrational modes.

In experiments using a mixture of $\text{KC}^{14}$N/$\text{KC}^{15}$N (1:1) as well as neon gas doped with a 1:1 $^{14}$N$_2$/$^{15}$N$_2$ mixture (Figure 3c), the higher band split into eight and the lower into six bands. In analogy with $\text{C}_2$ and $\text{C}_5$, a pattern of six isotopologues would be expected for the free $\text{N}_2^-$ anion or side-on $\text{KN}_2$ (Figure 1). The pattern of eight bands is indicative of three chemically inequivalent nitrogen atoms as in molecular end-on KNNN ($C_{ee}$, Figure 1). Thus the higher-frequency band at 2070.8 cm$^{-1}$ is assigned to the $v_1(N_2^-)$ stretch of molecular end-on KNN, which is in good agreement with the calculated band position (2124.5 cm$^{-1}$, CCSD(T)/ma-def2-TZVP), as well as with the predicted 14$\text{N}$ isotopic shifts (Table 2). The lower-frequency band at 1998.4 cm$^{-1}$ is in good agreement with the computed $v_1$ band position of side-on KN$_2$ (2038.8 cm$^{-1}$, CCSD(T)/ma-def2-TZVP) and close to the reported $v_1$ stretch of the free $\text{N}_2^-$ anion in solid nitrogen at 2006.5 cm$^{-1}$$^{[6a, 7]}$. The conversion of end-on KN$_2$ into the carrier of the 1998.4 cm$^{-1}$ band during UV irradiation ($\lambda = 273$ nm, Figure 3d) supports its assignment to side-on KN$_2$ rather than to free $\text{N}_2^-$.

The symmetric stretch of side-on KN$_2$ ($v_1$) has almost no IR intensity and, therefore, could not be observed in our experiments, while the corresponding mode of end-on KN$_2$ has some IR intensity and could be observed for end-on $\text{K}^{14}$N$_2$ and $\text{K}^{15}$N$_2$ in solid neon (Table 2, Figure 59, Supporting Information).

In solid nitrogen matrices no irradiation was needed to produce KN$_2$. After deposition the $^{14}$N stretch showed a strong band at 2048.5 cm$^{-1}$ with a site at 2049.3 cm$^{-1}$ for end-on K$^{14}$N$_2$ and the broad band of free $^{14}$N$_2^-$ as described by Michl and Andrews at 2003.5 cm$^{-1}$. Upon annealing to 25 K the band at 2048.5 cm$^{-1}$ increased drastically while the $\text{N}_2^-$ band decreased so that another band at 2006.5 cm$^{-1}$ became visible. The 2006.5 cm$^{-1}$ band has not been described by Michl or Andrews and is assigned to the antisymmetric azide stretch ($v_5$) of side-on KN$_2$ in solid nitrogen. In the mixed isotope experiment where laser ablated KC$^{14}$N/KC$^{15}$N (1:1) was co-deposited with pure $^{14}$N$_2$/$^{15}$N$_2$ (1:1) at 12 K (Figure 57, Supporting Information), the band at 2048.5 cm$^{-1}$ split into an octet, whereas the band at 2006.5 cm$^{-1}$ split into a sextet, as expected for end-on and side-on KN$_2$ (Figure 57b, Supporting Information). Upon irradiation with UV light ($\lambda = 273$ nm) the free $\text{N}_2^-$ band was depleted, while the 2048.5 and 2006.5 cm$^{-1}$ bands were not (Figure 57c, Supporting Information). All calculated and observed experimental band positions of the asymmetric $\text{N}_2^-$-stretches of side-on and end-on KN$_2$ in Ne, Ar, and N$_2$ are displayed in Table 2.

Calculations at the CCSD(T)/ma-def2-TZVP level of theory predict that side-on KN$_2$ is 3.5 kJ mol$^{-1}$ lower in energy than end-on KN$_2$. 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 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 ($\lambda = 470$ nm)

![Figure 4](https://www.chemeurj.org/)

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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 KN$_2$ is the main product after $\lambda = 470$ nm photoysis.

In principle, three reaction mechanisms can be considered for the formation of molecular KN$_2$ in the experiments described above: i) recombination of K$^+$ and N$_2^-$ ions, ii) reaction of potassium atoms and N$_2$ radicals, and iii) reaction of potassium nitrene (KN) and N$_2$ molecules [Eq. (1)]. In the neon and argon experiments, however, the former two reactions can be ruled out since neither N$_2^-$ ions nor N$_2$ radicals were observed in these matrices. KN is calculated to have a triplet ground state (MRCI(+Q))$^{13}$ while the reaction of KN + N$_2$ (1) is assumed to proceed with excited singlet 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 cm$^{-1}$)$^{14}$ 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 KN$_2$.

$$\text{KN} + \text{N}_2 \rightarrow \text{KN}_2$$

In solid nitrogen, large amounts of end-on KN$_2$ and only small amounts of side-on KN$_2$ were observed after annealing to 25 K. At the same time high amounts of free N$_2^-$ were consumed during this process, suggesting that KN$_2$ might also be formed by a recombination of K$^+$ and N$_2^-$ ions in solid nitrogen. This observation explains the high abundance of end-on compared to side-on KN$_2$ in solid nitrogen: The partial negative charges on the two terminal nitrogen atoms in N$_2^-$ favor an electrostatic recombination of K$^+$ and N$_2^-$ and the formation of the thermodynamically less stable end-on KN$_2$.

Figure 5 shows the $^{14}$N isotopic IR band patterns obtained after co-deposition of laser ablated KCN with $^{15}$N$_2$ doped neon (a) and of KC$^{14}$N with $^{14}$N$_2$ doped neon (b) after irradiation with blue light ($\lambda = 470$ nm). Obviously, spectra Figure 5a and b are complementary. Due to the purity of 98 atom % $^{15}$N of the KC$^{13}$N used for the experiment, traces of the K$^{14}$N$^{14}$N$^{15}$N isotope can be observed in Figure 5b. The high yield of K$^{13}$N$_2$ in Figure 5b is probably due to formation of side-on KN (1) is not only to form KN$^{14}$N and KN$^{15}$N$^{15}$N in solid KCl$^{15}$N. The absence of any ($^{14}$N$^{14}$N$^{15}$N) isotopologues in Figure 5b and of ($^{14}$N$^{14}$N$^{15}$N$^{15}$N), and KN$^{14}$N$^{14}$N$^{14}$N isotopologues in Figure 5a implies the absence of a reaction between KN$^{15}$N and KN$^{15}$N$^{14}$N producing KN$^{14}$N$^{14}$N$^{14}$N or vice versa. On the other hand, K$^{15}$N$_2$ can react with $^{14}$N$_2$ not only to form the addition product KN$^{14}$N$^{14}$N$^{15}$N but also to form KN$^{14}$N$^{14}$N$^{15}$N and KN$^{14}$N$^{14}$N$^{14}$N$^{15}$N. This observation may indicate a KN$^{14}$N$_2$ ion-pair/intermediate or transition state involving a cyclic $^{14}$N$_2$ 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 N$_2$ has already been postulated by Michl and co-workers.$^{160}$

In addition to the free C$^-$ and N$_2^-$ anions and the ion pairs KC$^{14}$N and KN$_2$, 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 C$^{12}$N$_2$, NC$^{14}$N$^{13}$N, and CN$^{14}$N$^{15}$N radicals (for further details and a discussion of the reaction mechanisms see the Supporting Information).

$$\text{K}^{14}\text{N}^+ + \text{N}_2^- \rightarrow \text{K}^+ \text{N}^{14}\text{N}^+ \text{N}^+$$

(2)

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 KN$_2$ and KC$_2$ are reported for the first time. To the best of our knowledge, previous IR spectroscopic studies on potassium azide were performed only on crystalline KN$_2$ while several studies were reported on molecular group $^2$[15] group 13,$^{15}$ and transition-metal azides.$^{17}$ The ion pair KN$_2$ exists in an end-on and a side-on form, which are separated by a barrier of about 12 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 (KN), that reacts photochemically with dinitrogen to molecular potassium azide (KN$_2$). Laser ablation of KN$_2$ 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 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

[1] R. L. Pulliam, C. Savage, M. Agúndez, J. Cernicharo, M. Guélin, L. M. Ziurys, Astrophys. J. 2010, 725, L181 –L185.
[2] K. Ishii, T. Taketsugu, K. Yamashita, J. Chem. Phys. 2007, 127, 194307.
[3] a) E. Hirota, Bull. Chem. Soc. Jpn. 1995, 68, 1 –16; b) J. Xin, L. M. Ziurys, J. Chem. Phys. 1999, 110, 4797 –4802.
[4] a) F. A. Redeker, H. Beckers, S. Riedel, Chem. Commun. 2017, 53, 12958 –12961; b) F. A. Redeker, H. Beckers, S. Riedel, RSC Adv. 2015, 5, 106568 –106573.
[5] a) J. Szczepanski, S. Ekern, M. Vala, J. Phys. Chem. A 1997, 101, 1841 –1847; b) J. Szczepanski, C. Wehlburg, M. Vala, J. Phys. Chem. A 1997, 101, 7039 –7042.
[6] a) R. Tian, J. C. Facelli, J. Michlı, J. Phys. Chem. 1988, 92, 4073 –4079; b) R. Tian, V. Balaji, J. Michlı, J. Am. Chem. Soc. 1988, 110, 7225 –7226.
[7] M. Zhou, L. Andrews, J. Phys. Chem. A 2000, 104, 1648 –1655.
[8] L. Andrews, M. Zhou, G. V. Chertihin, W. D. Bare, J. Phys. Chem. A 2000, 104, 1656 –1661.
[9] a) Z. K. Ismail, R. H. Hauge, J. L. Margrave, J. Mol. Spectrosc. 1973, 45, 304 –315; b) Z. K. Ismail, R. H. Hauge, J. L. Margrave, J. Mol. Spectrosc. 1975, 54, 402 –411.
[10] D. Forney, W. E. Thompson, M. E. Jacox, J. Chem. Phys. 1992, 97, 1664 –1674.
[11] H. Wang, G. Li, Eur. Phys. J. D 2014, 68, 182.
[12] W. Weltner, P. N. Walsh, C. L. Angell, J. Chem. Phys. 1964, 40, 1299 –1305.
[13] a) R. L. DeKock, W. Weltner, J. Am. Chem. Soc. 1971, 93, 7106 –7107; b) D. E. Milligan, M. E. Jacox, J. Chem. Phys. 1966, 44, 2850 –2856.
[14] N. G. Moll, W. E. Thompson, J. Chem. Phys. 1966, 44, 2684 –2686.
[15] H. A. Papazian, J. Chem. Phys. 1961, 34, 1614 –1616.
[16] C. R. Brazier, P. F. Bernath, J. Chem. Phys. 1988, 88, 2112 –2116.
[17] A. Citra, X. Wang, W. D. Bare, L. Andrews, J. Phys. Chem. A 2001, 105, 7799 –7811.

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