

Infrared spectra of ClCN^+ , CINC^+ , and BrCN^+ trapped in solid neonMarilyn E. Jacox^{a)} and Warren E. Thompson^{b)}*Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8441*

(Received 5 March 2007; accepted 11 May 2007; published online 29 June 2007)

When a mixture of ClCN or BrCN with a large excess of neon is codeposited at 4.3 K with a beam of neon atoms that have been excited in a microwave discharge, the infrared spectrum of the resulting solid includes prominent absorptions of the uncharged isocyanide, ClNC or BrNC , and of the corresponding cation, ClCN^+ or BrCN^+ . The NC-stretching fundamentals of the isocyanides trapped in solid neon lie close to the positions for their previously reported argon-matrix counterparts. The CN-stretching absorptions of ClCN^+ and BrCN^+ and the CCl-stretching absorption of ClCN^+ appear very close to the gas-phase band centers. Absorptions of two overtones and one combination band of ClCN^+ are identified. Reversible photoisomerization of ClCN^+ to CINC^+ occurs. The two stretching vibrational fundamentals and several infrared and near infrared absorptions associated with electronic transitions of CINC^+ are observed. Minor infrared peaks are attributed to the vibrational fundamental absorptions of the CX and CX^+ species ($X=\text{Cl, Br}$).

[DOI: 10.1063/1.2746868]

I. INTRODUCTION

Because the CN group, like the halogen atom, possesses several low-lying excited states, the energy level patterns of the halogen cyanides resemble those of the diatomic halogen molecules. However, the halogen cyanides may also photoisomerize to form isocyanides. Milligan and Jacox¹ reported that the 122 nm irradiation of ClCN trapped in solid argon produces CINC , evidenced by the appearance of its NC-stretching absorption in the infrared spectrum of the deposit. Photoisomerization of HCN and of BrCN to form the corresponding isocyanides also occurred. Subsequently, the photoisomerization of FCN was reported.²

Although the HCN-HNC isomerization is now familiar, that of the halogen-substituted species has received little attention. Lee and Racine³ conducted high-level *ab initio* calculations of the vibrational fundamentals of CINC and FNC , indicating that CINC is 42.7(1.0) kcal/mol, or 178.7(4.2) kJ/mol, higher in energy than ClCN . Their value for the ground-state CN-stretching fundamental of CINC , 2098(86) cm^{-1} , agreed well with the observed value, but the tentative assignment of a very weak absorption in the argon-matrix experiments to the NCl-stretching fundamental was not supported. Lee *et al.*⁴ refined these results by conducting additional calculations with correlation-consistent basis sets and by evaluating the anharmonic constants.

The vibrational and electronic energy levels of ClCN^+ and BrCN^+ are relatively well known. Early studies of the photoelectron spectra of these species by Heilbronner *et al.*⁵ and by Lake and Thompson⁶ established that both ClCN^+ and BrCN^+ have two low-lying electronic states. The $\bar{A}^2\Sigma^+$ state appears in the near infrared and the $\bar{B}^2\Pi$ state in the visible spectral region. This indicates that configuration in-

teraction plays an important role in the chemical bonding of the halogen cyanide cations. The XCN^+ species were among the first triatomic cations to yield spectral data. These early studies considerably refined the spectroscopic constants available from the photoelectron studies. Allan and Maier⁷ observed electron-excited emission arising from two electronic transitions each of XCN^+ ($X=\text{Cl, Br, and I}$) in the spectral region between 400 and 900 nm. Concurrently, Eland *et al.*⁸ used coincidence measurements to study quantum yields and fluorescence lifetimes for these species. Several more recent experimental and theoretical studies, to be considered later, yielded detailed vibrational assignments for these cations in their ground and two lowest excited electronic states. However, similar data have not been reported for the corresponding XNC^+ isomers.

Experiments in our laboratory have explored the spectroscopy and photochemistry of a number of small molecular ions. As in earlier studies which have yielded infrared spectroscopic data for many small molecular ions trapped in solid neon,⁹ the species or mixture of interest, contained in a large excess of neon, is introduced into the system downstream from a quartz tube in which pure neon is excited in a microwave discharge. Excited neon atoms and their resonance radiation interact with the resulting mixture, which is then frozen onto an observation surface maintained at 4.3 K. The effective energy is that of the lowest excited states of neon atoms, between 16.6 and 16.85 eV, and very little backstreaming of molecules into the discharge region occurs. In one of these studies,¹⁰ the molecule of interest was HCN . Although HNC was among the principal products, a sufficient concentration of HCN^+ was stabilized for identification of its ground-state CH-stretching fundamental absorption. When the deposit was exposed for a few minutes to radiation of wavelength longer than 850 nm, the HCN^+ photoisomerized to HNC^+ , for which all three vibrational fundamentals were identified. The reverse photoisomerization occurred

^{a)}Guest researcher.^{b)}Technology Administration, U.S. Department of Commerce.

when the matrix-isolated HNC^+ was then exposed to radiation of wavelength shorter than 580 nm. Recently, we studied the photoionization of NCCN .¹¹ The spectrum of the initial deposit included absorptions of the previously identified isomers CNCN and CNNC , as well as prominent absorptions of NCCN^+ . The reversible photoisomerization of NCCN^+ to CNCN^+ occurred, and two infrared absorptions of CNCN^+ were identified. The wealth of new information which was obtained from the experiments on HCN and on NCCN suggested that similar experiments on CICN and BrCN might help to fill in some of the gaps in our knowledge of the spectroscopy and photochemistry of ions derived from the halogen cyanides. This paper reports the results of that study.

II. EXPERIMENTAL DETAILS

The CICN (Matheson Co., Inc.) sample¹² used in these experiments had been freed of residual CO_2 by condensation in a dry ice-acetone cooled trap and pumping on the solid deposit. The BrCN sample (Aldrich Chemical Co.) was purified by vacuum distillation. Gas mixtures with the neon-matrix gas (Spectra Gases, Inc., Research Grade, 99.999%) were prepared using standard vacuum procedures. Samples with Ne: CICN mole ratios ranging from 400:1 to 3200:1 and with Ne: BrCN mole ratios ranging from 200:1 to 800:1 were studied.

The sample mixtures were codeposited at 4.3 K with a similar amount of pure neon that had been excited by a microwave discharge before streaming through a 1 mm pinhole in the end of a quartz discharge tube. Details of the deposition procedure and of the discharge configuration have been described previously.^{10,13} (The pure neon was not passed through a Nanochem filter in this series of experiments.)

The absorption spectra of the sample deposits were obtained using a Bomem DA 3.002 Fourier-transform interferometer with transfer optics that have been described previously.¹⁴ Most of the observations were conducted with a resolution of 0.2 cm^{-1} between 450 and 5000 cm^{-1} using a global source, a KBr beam splitter, and a wide band HgCdTe detector cooled to 77 K. Observations for several samples were conducted at the same resolution between 1700 and 8500 cm^{-1} using a CaF_2 beam splitter and an InSb detector cooled to 77 K. Data were accumulated for each spectrum over a period of at least 15 min. The resulting spectrum was ratioed against a similar one taken without a deposit on the cryogenic mirror. Under these conditions, the positions of the prominent, nonblended atmospheric water vapor lines between 1385 and 1900 cm^{-1} and between 3620 and 3900 cm^{-1} , observed in a calibration scan using the KBr beam splitter and HgCdTe detector, agreed to within 0.01 cm^{-1} with the high resolution values reported by Toth.¹⁵ The frequencies of absorptions between 1700 and 5000 cm^{-1} observed using the CaF_2 beam splitter and InSb detector agreed with those obtained in the experiments using the KBr beam splitter and HgCdTe detector. Based on previous investigations, with this experimental configuration the standard uncertainty (type B) in the determination of the positions of the absorption maxima for molecules trapped in solid neon is $\pm 0.1\text{ cm}^{-1}$ (coverage factor, $k=1$, i.e., 1σ).

Information on photoinduced changes in the matrix sample was obtained by exposing the deposit to various wavelength ranges of near infrared, visible, and ultraviolet radiation. For the Ne: CICN samples, a tungsten background source was used with a filter of Schott glass type RG1000 or of Corning glass type 2403, 2408, 2424, 3480, or 3484 to remove radiation of wavelength shorter than approximately 1000, 630, 610, 580, 560, or 520 nm, respectively. For irradiation at shorter wavelengths, a medium-pressure mercury-arc source was used with a filter of Corning glass type 3389, 3060, 7380, or 7740 to exclude radiation of wavelength shorter than approximately 420, 370, 345, or 280 nm, respectively. One experiment was also conducted using a filter of Corning glass type 5970, which transmits radiation of wavelength between 410 and 310 nm. For the Ne: BrCN samples, the tungsten background source was used with a filter of Schott glass type RG850, RG780, or RG 695 or with a filter of Corning glass type 2403 or 2424 to remove radiation of wavelength shorter than approximately 850, 780, 695, 630, or 580 nm, respectively. For that system, the medium-pressure mercury-arc source was used with a filter of Corning glass type 3384, 3389, 7380, or 7740 to exclude radiation of wavelength shorter than approximately 490, 420, 345, or 280 nm, respectively. For both Ne: CICN and Ne: BrCN samples, some irradiations were also conducted using the mercury-arc source without a filter, with a cutoff wavelength near 250 nm.

III. RESULTS AND DISCUSSION

A. Production and photoisomerization of CICN^+

The positions and approximate relative intensities of the new absorptions which appear in Ne: CICN samples that have been codeposited with a beam containing excited neon atoms and their resonance radiation are summarized in Table I. Spectral regions of especial interest between 450 and 4000 cm^{-1} in these experiments are shown in the traces labeled (a) in Fig. 1. Most of the peaks present in the experiment on the sample with the higher concentration of CICN (Ne: $\text{CICN}=800:1$) are present even in the experiment on the more dilute (Ne: $\text{CICN}=3200:1$) sample, indicating that molecular aggregation is a minor process.

The strongest product absorption, at 2080.5 cm^{-1} , is readily assigned to CINC , which was first produced¹ by the 122 nm irradiation of Ar: CICN samples. In the earlier argon-matrix experiments, the NC-stretching absorption of CINC appeared at 2074 cm^{-1} .

Fragmentation of CICN , which could result from backstreaming of that molecule into the discharge tube, is a minor process. The moderately intense pair of absorptions between 2043 and 2048 cm^{-1} can be assigned to CN .¹⁰ These two peaks grow on unfiltered mercury-arc irradiation of the deposit. In a measurement of a Ne: $\text{NCCN}=800:1$ deposit,¹¹ the strongest absorption of NCCN was at 2160.2 cm^{-1} . No absorption appears near that position in the Ne: CICN experiments. However, the infrared spectrum of the Ne: $\text{CICN}=800:1$ sample includes a weak absorption at 2303.4 cm^{-1} , attributable to the most intense infrared absorption of the CNCN isomer.¹⁶ The diode laser study by Yamada *et al.*¹⁷

TABLE I. New absorptions (cm^{-1}) which appear between 500 and 8500 cm^{-1} when a Ne:C₁CN mixture is codeposited at 4.3 K with a beam of excited neon atoms. Based on previous investigations, the standard uncertainty (type B) in the frequency measurement is $\pm 0.1 \text{ cm}^{-1}$ (coverage factor, $k=1$, i.e., 1σ). vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad; and sh, shoulder. The irradiation studies in the Ne:C₁CN=3200:1 experiment used a 580 nm cutoff filter, while those in the Ne:C₁CN=800:1 experiment used a 520 nm cutoff filter. A, change in intensity on irradiation of the deposit, $\lambda > 580$ or 520 nm. B, change in intensity on irradiation of the deposit, $\lambda > 345 \text{ nm}$.

Ne:C ₁ CN=3200:1	Ne:C ₁ CN=800:1	Assignment
626.5w		
642.8w, A+B-	642.8wm, A+B-	C ₁ CN ⁺ $2\nu_2$
726.6vw, A-B+	726.4vw, A-B+	³⁷ C ₁ CN ⁺ ν_3
734.7w, A-B+	734.8w, A-B+	³⁵ C ₁ CN ⁺ ν_3
	816.0wm, B-	
823.4wm, A+B-	823.4m, A+B-	³⁷ C ₁ CN ⁺ ν_3
831.8m, A+B-	832.0ms, A+B-	³⁵ C ₁ CN ⁺ ν_3
860.6wm	860.5w	C ³⁷ Cl
866.4m	866.7wm	C ³⁵ Cl
	971.0w, B+	
	974.9w, B+	
1160.8w		C ³⁷ Cl ⁺
1162.4w	1162.7w	C ³⁷ Cl ⁺
1168.9wm		C ³⁵ Cl ⁺
1170.4wm	1170.7wm	C ³⁵ Cl ⁺
	1459.7vw, A-B+	³⁵ C ₁ CN ⁺ $2\nu_3$
1616w,br	1609w,br, A-B+	C ₁ CN ⁺
1703.9wm		
1919.7s, A+B-	1919.4vs, A+B-	C ₁ CN ⁺ ν_1
1952.7vw, A-B+	1952.8vw, A-B+	C ₁ CN ⁺ ν_1
2043.8ms, C	2043.6m, C	CN
2047.2ms, C	2047.5s, C	CN
2054.1w, B+	2054.0w, B+	CN ⁻
2062.3ms, B-	2062.2ms, B-	
2080.5vs, B+	2080.5vs, B+	C ₁ CN ν_1
	2195.8wm, B+	
	2205.3wm, B+	
	2206.3sh, B+	
	2303.4w, B+	CNCN
	2326.8m, B-	
	2331.1m, B-	
	2357.1w, B+	
	2358.8vw, B+	
	2748.2vw, A+B-	C ₁ CN ⁺ ($\nu_1 + \nu_3$)
	3253.9w, B+	
	3330.6vw, B+	
3814.1m, A+B-	3814.1m, A+B-	C ₁ CN ⁺ $2\nu_1$
	4142vw, br, A-B+	C ₁ CN ⁺
	4490vw, br, A-B+	C ₁ CN ⁺
4680vw, A-B+	4680w, br, A-B+	C ₁ CN ⁺
	5344vw, br, A-B+	C ₁ CN ⁺
	6956vw, br, A-B+	C ₁ CN ⁺

determined that $\Delta G_{1/2}$ of C³⁵Cl lies at $866.086(18) \text{ cm}^{-1}$. A weak to moderately intense absorption at 866.7 cm^{-1} in the Ne:C₁CN=800:1 experiment corresponds very well with the expected position of the C³⁵Cl absorption. A weaker absorption appears at 860.5 cm^{-1} , very close to the calculated position (860.7 cm^{-1}) for C³⁷Cl, present in approximately 25% natural abundance. Like the pair of absorptions attributed to the CN fragment, these two peaks grow on unfiltered

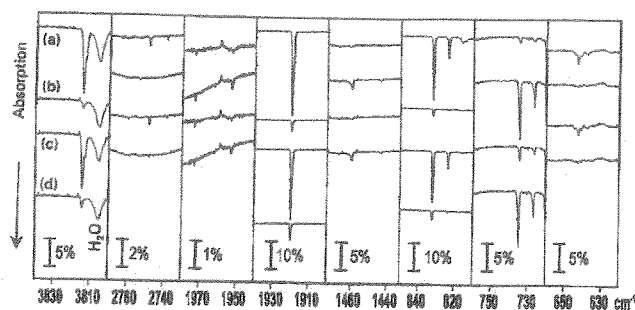


FIG. 1. Reversible photoisomerization of C₁CN⁺. 16.4 mmol Ne:C₁CN=800:1 codeposited at 4.3 K over a period of 268 min with 9.93 mmol Ne that had been passed through a microwave discharge. (a) Initial deposit, (b) 20 min mercury-arc irradiation, $\lambda > 345 \text{ nm}$, (c) 45 min tungsten-lamp irradiation, $\lambda > 520 \text{ nm}$, and (d) 20 min mercury-arc irradiation, $\lambda > 580 \text{ nm}$.

mercury-arc irradiation of the deposit. The CCl peaks are somewhat more prominent in the Ne:C₁CN=3200:1 experiment, suggesting that fragmentation is more important for the highly dilute sample.

The behavior of the product spectra when the deposit was subsequently exposed to near ultraviolet and visible radiation is also summarized in Table I, and absorptions observed in spectral regions of particular interest are shown in traces (b)–(d) of Fig. 1. On filtered mercury-arc irradiation of the deposit with radiation of wavelength shorter than approximately 370 nm, product absorptions at 642.8, 823.4, 831.8, 1919.7, 2748.2, and 3814.1 cm^{-1} decrease greatly in intensity but are almost completely regenerated when the sample is subsequently exposed for a few minutes to tungsten-lamp radiation of wavelength shorter than approximately 630 nm. This cycle can be repeated, with similar results. These peaks are irreversibly destroyed by exposing the deposit to unfiltered mercury-arc radiation. Their carrier, which will be identified later in this discussion, is designated here as species I.

As species I experiences photodestruction, new sharp absorptions, shown in trace (b) of Fig. 1, appear at 726.6, 734.7, 1459.7, and 1952.7 cm^{-1} . These are accompanied by a new broad absorption with maximum near 1610 cm^{-1} , shown in trace (b) of Fig. 2, and by broad absorptions with maxima near 4142, 4490, 4680, 5344, and 6956 cm^{-1} , shown in trace (b) of Fig. 3. The structure between 1595 and 1635 cm^{-1} , present in all of the traces of Fig. 2, and the

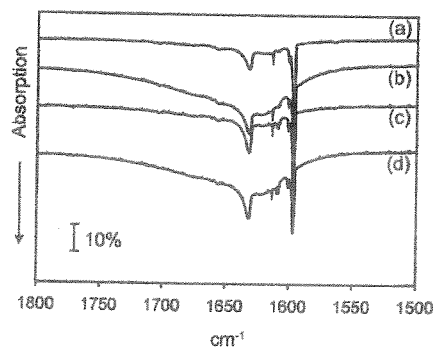


FIG. 2. Broad bands formed during reversible photoisomerization of C₁CN⁺ (see Fig. 1).

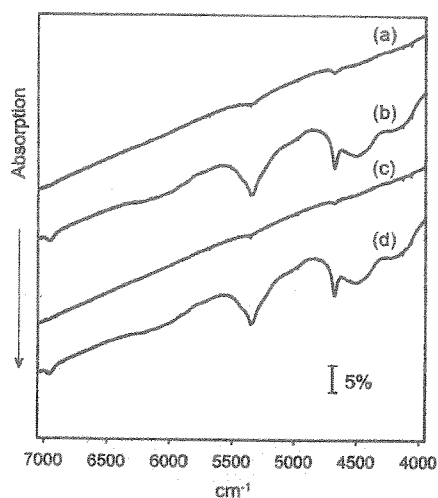


FIG. 3. Near infrared absorptions associated with the reversible photoisomerization of CICN^+ . 12.1 mmol Ne: CICN =800:1 codeposited at 4.3 K over a period of 222 min with 11.8 mmol Ne that had been passed through a microwave discharge. (a) Initial deposit, (b) 20 min mercury-arc irradiation, $\lambda > 345$ nm, (c) 50 min tungsten-lamp irradiation, $\lambda > 560$ nm, and (d) 20 min mercury-arc irradiation, $\lambda > 345$ nm.

absorption at 3783 cm^{-1} in Fig. 1 are contributed by rotating and nonrotating H_2O ,¹⁸ which is desorbed from the walls of the deposition system during preparation of the matrix sample. As is shown in traces (c) of Figs. 1–3, the carrier of the new sharp and broad absorptions, designated as species II, is destroyed as species I is regenerated. Traces (d) of Figs. 1–3 demonstrate that the photodestruction of species II is also reversible. However, species II, like species I, is irreversibly destroyed by exposing the deposit to unfiltered mercury-arc radiation.

A few other unidentified product absorptions, the most prominent of which lies at 2062.6 cm^{-1} , change irreversibly on exposure of the deposit to visible or near ultraviolet radiation.

Consideration of the energetics of the various dissociative ionization processes suggests that CICN^+ , but not its fragment ions, can be formed below the high-energy limit of the first set of excited energy levels of the neon atom, 16.85 eV. The photoionization experiments of Dibeler and Liston¹⁹ gave a value of 12.34(1) eV for the first ionization energy of CICN . Later photoelectron spectroscopic studies^{5,6} gave a similar value. The electron impact study of CICN by Herron and Dibeler²⁰ yielded an appearance energy of 17.2(2) eV for CCl^+ . The gas-phase emission spectroscopic study by Bredohl *et al.*²¹ confirmed that the carrier of the bands attributed to CCl^+ in the diatomic molecule compilation of Huber and Herzberg²² is indeed contributed by that species, with a ground-state 1-0 band separation of 1165 cm^{-1} . Two pairs of peaks between 1160 and 1171 cm^{-1} which are destroyed by exposure of the deposit to unfiltered mercury-arc radiation can be assigned to CCl^+ trapped in two different sites in the solid. The calculated isotopic separation between C^{35}Cl^+ and C^{37}Cl^+ is 8.1 cm^{-1} , and the observed isotopic separations for the two pairs of peaks are 8.0 and 8.1 cm^{-1} , in excellent agreement. The appearance of CCl^+ in the present experiments can be attributed to the photoioniza-

tion of the initially formed CCl . Dibeler and Liston measured a value of 17.32(2) eV for the appearance energy of Cl^+ from CICN . This value is 4.98 eV ($40\,200\text{ cm}^{-1}$) above the appearance energy of ground-state CICN^+ , implying that radiation of wavelength longer than 249 nm should not dissociate CICN^+ into Cl^+ + CN . Finally, Dibeler and Liston measured an appearance energy of 18.50(2) eV for the production of CN^+ from CICN . This energy is 6.16 eV ($49\,700\text{ cm}^{-1}$) above the appearance energy of the ground state of CICN^+ , implying that radiation of wavelength longer than 201 nm should not dissociate CICN^+ into Cl^+ + CN^+ .

Wang *et al.*²³ calculated the molecular properties of the \tilde{X} and \tilde{A} states of CICN^+ at various computational levels. Their MP2 calculations gave an inadequate description of this species. The best results were achieved in their most elaborate calculations, at the CCSD(T)/6-311G(2d) level, which gave the harmonic stretching vibrational fundamentals of ground-state CICN^+ , $\nu_{\text{CN}}=1959.8\text{ cm}^{-1}$ and $\nu_{\text{CCl}}=800.2\text{ cm}^{-1}$. The degeneracy of the bending fundamental was split, with values of 315.3 and 375.2 cm^{-1} . Since ground-state CICN^+ is linear, this splitting was attributed to inadequacy of the unrestricted Hartree-Fock wave function for describing the degenerate ${}^2\Pi$ state. Recently, Mishra *et al.*²⁴ calculated the vibrational structure of the first photoelectron band of CICN , assuming that the ground state of CICN^+ does not interact with its excited electronic states. Their B3LYP/aug-cc-pVTZ calculations gave $\nu_{\text{CN}}=1988\text{ cm}^{-1}$, $\nu_{\text{bend}}=366\text{ cm}^{-1}$, and $\nu_{\text{CCl}}=821\text{ cm}^{-1}$ for ground-state CICN^+ . In accord with standard spectroscopic notation, in the subsequent discussion these vibrational fundamentals will be designated as ν_1 , ν_2 , and ν_3 , respectively.

Except for a single study by Leutwyler *et al.*²⁵ of the $\tilde{B}-\tilde{X}$ absorption band system of CICN^+ trapped in a neon matrix, all of the spectroscopic observations of that species have been in the gas phase. The earliest work⁷ and later optical and photoelectron spectroscopic studies^{26–28} have consistently determined a ground-state spin splitting of $-276(2)\text{ cm}^{-1}$. The electron-excited fluorescence experiments by Fulara *et al.*²⁶ and Greiman *et al.*²⁷ located the band center for the CN-stretching fundamental at $1915(2)\text{ cm}^{-1}$ and that of the CCl-stretching fundamental at $827(2)\text{ cm}^{-1}$. The laser excitation measurements by Celii *et al.*²⁹ required reassignment of the origin of the \tilde{B} state of CICN^+ but did not change the vibrational separations associated with the two stretching fundamentals.

The prominent species I absorption at 1919.7 cm^{-1} and the pair of species I absorptions at 831.8 and 823.4 cm^{-1} lie very close to the CN- and CCl-stretching fundamentals, respectively, of gas-phase CICN^+ . The relative intensities of the two latter absorptions and their frequency separation are appropriate for the assignment of the 831.8 cm^{-1} absorption to ${}^{35}\text{CICN}^+$ and of the 823.4 cm^{-1} absorption to ${}^{37}\text{CICN}^+$. The bending fundamental, ν_2 , lies at too low a frequency to be accessible in the present experiments.

The first photoelectron band of CICN , recorded by Holland *et al.*,²⁸ included a peak at $2735(10)\text{ cm}^{-1}$, attributed to the $\nu_1+\nu_3$ combination band of ground-state CICN^+ . This peak agrees well with the position of the weak neon-matrix

absorption at 2748.2 cm^{-1} in the present study. Similarly, Holland *et al.* attributed a peak at $3792(10)\text{ cm}^{-1}$ to $2\nu_1$ of ClCN^+ , compared to the neon-matrix value of 3814.1 cm^{-1} . These correspondences strongly support the identification of species I as ClCN^+ .

The species I absorption at 642.8 cm^{-1} does not have a counterpart in the gas-phase spectrum of ground-state ClCN^+ . Because ClCN^+ is linear in its ground state and in both of its observed excited electronic states, very few data are available for the bending vibration energy levels of the molecule. The reassignment of the $\tilde{B}-\tilde{X}$ spectrum proposed by Celii *et al.*²⁹ led to their tentative assignment of a peak 756 cm^{-1} below the band origin to $2\nu_2$ of ground-state ClCN^+ . Because the 642.8 cm^{-1} infrared absorption of ClCN^+ is lower in frequency than either of the two stretching fundamentals, it must be associated with the bending fundamental. Its magnitude is also appropriate for $2\nu_2$ of the cation. In the absence of data for the ν_2 fundamental, the expectation that it should be split by Renner-Teller interaction has not previously been considered. However, $2\nu_2$ of ClCN^+ should have two components of Π vibronic symmetry. In rare-gas matrices, the lowest Renner-Teller component of a vibration generally shows the most prominent infrared absorption. Possibly the 756 cm^{-1} spacing of ground-state ClCN^+ arises from the higher frequency Π component of $2\nu_2$ and the 642.8 cm^{-1} absorption from the lower frequency component.

B. Spectrum of CINC^+

Various observations support the photoisomerization of ClCN^+ to form CINC^+ . Exposure of ClCN^+ to the mercury-arc radiation passed by a 345 nm cutoff filter is more than sufficient for excitation of the cation to its $\tilde{B}^2\Pi$ state. The gas-phase band origin for that state^{26,28-30} is well established to lie at $22\,515.54\text{ cm}^{-1}$, which corresponds to approximately 444 nm . Absorption bands of this transition have been observed out to 365 nm , and in the photoelectron studies by Holland *et al.*²⁸ excitation of the CCl-stretching vibration extended to $\nu=12$, corresponding to approximately 350 nm . The neon-matrix absorption study²⁵ of this transition of ClCN^+ also showed a long progression in the CCl-stretching vibration. Maier *et al.*³¹ reported photoelectron-fluorescence coincidence measurements of electronic transitions of several molecular cations, including the \tilde{B} state of ClCN^+ . They found biexponential fluorescence from this state. The photoion-fluorescence coincidence study by Braitbart *et al.*³² confirmed the biexponential behavior of fluorescence from the \tilde{B} state of ClCN^+ . These results would be consistent with the photoisomerization of ClCN^+ in its $\tilde{B}^2\Pi$ state to form CINC^+ , a species which has not previously been identified.

The positions of the sharp absorptions of species II are appropriate for their contribution by CINC^+ . The approximate relative intensities of the species II peaks at 734.7 and 726.6 cm^{-1} , shown in traces (b) and (d) of Fig. 1, and the magnitude of their separation are consistent with their proposed assignment to the NCl-stretching fundamental, ν_3 , of the two chlorine-isotopic species of CINC^+ . If CINC^+ is con-

sidered to approximate a diatomic molecule in which the Cl atom vibrates against an atom of mass 26 and the Cl-N stretching absorption of $^{35}\text{CINC}^+$ is assumed to lie at 734.7 cm^{-1} , the calculated position of the corresponding $^{37}\text{CINC}^+$ vibration would equal 726.2 cm^{-1} , compared to the observed value of 726.6 cm^{-1} . The weak absorption at 1459.7 cm^{-1} , also shown in traces (b) and (d) of Fig. 1, lies close to the position expected for the first overtone of the NCl-stretching fundamental of CINC^+ . This absorption is too weak for detection of its $^{37}\text{CINC}^+$ counterpart. Finally, the very weak, sharp absorption at 1952.8 cm^{-1} in traces (b) and (d) of Fig. 1 may have been contributed by the NC-stretching fundamental (ν_1) of CINC^+ .

Several very broad absorptions shown in traces (b) and (d) of Figs. 2 and 3, with maxima at approximately 1610 , 4142 , 4490 , 4680 , 5344 , and 6956 cm^{-1} , also have photodestruction behavior appropriate for their assignment to CINC^+ . Because of the enhanced contribution of phonon interactions to electronic transitions of matrix-isolated molecules, typically they are much broader than vibrational transitions. Thus, these bands probably arise from one or more low-lying electronic transitions of CINC^+ . That species, like ClCN^+ , is expected to possess at least two such transitions, implying that configuration interaction plays a very important role for both ClCN^+ and CINC^+ .

C. Infrared spectrum of BrCN^+

The positions and approximate relative intensities of the product absorptions which appear between 500 and 5000 cm^{-1} on codeposition of a Ne:BrCN sample with a beam of excited neon atoms are summarized in Table II, and portions of the absorption spectrum of a typical sample are shown in Fig. 4. Once again, the uncharged isomer contributes a prominent absorption; the NC-stretching absorption of BrNC is readily identified at 2072.2 cm^{-1} , close to the 2067 cm^{-1} absorption assigned to BrNC in the earlier argon-matrix study.¹ That peak diminished in intensity on subsequent unfiltered mercury-arc irradiation of the deposit, as did the 2072.2 cm^{-1} peak and several other peaks which are labeled by filled circles in Fig. 4.

Fragmentation remains a minor process in the Ne:BrCN experiments, although it occurs to a somewhat greater extent than in the Ne:ClCN studies. As in the latter studies, absorptions attributable to CN were observed between 2043 and 2048 cm^{-1} . The infrared diode laser study by Marr *et al.*³³ assigned the $J(1.5\leftarrow 0.5)$ transition in the 1-0 vibrational band of ground-state C^{79}Br at 723.9 cm^{-1} . A pair of moderately intense absorptions at 722.7 and 723.2 cm^{-1} in the Ne:BrCN experiments lie close to the positions of the CBr-stretching absorptions of the two bromine-isotopic species of CBr. However, the calculated frequency separation is 1.2 cm^{-1} , approximately twice the observed separation, which may, alternatively, arise from the trapping of CBr in two different types of site in the neon solid.

The behavior of Ne:BrCN samples on codeposition with discharged neon is summarized in Table II for a Ne:BrCN = 800:1 experiment. In that study, the first filtered mercury-arc irradiation employed a 420 nm cutoff filter, which was

TABLE II. New absorptions (cm^{-1}) which appear between 500 and 5000 cm^{-1} when a Ne:BrCN=800:1 mixture is codeposited at 4.3 K with a beam of excited neon atoms. Based on previous investigations, the standard uncertainty (type B) in the frequency measurement is $\pm 0.1 \text{ cm}^{-1}$ (coverage factor, $k=1$, i.e., 1σ). vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad; and sh, shoulder. A, changes in intensity on mercury-arc irradiation. $\lambda > 420 \text{ nm}$. B, changes in intensity on unfiltered mercury-arc irradiation.

Ne:BrCN=800:1	Assignment
608.6w, B-	
610.2w, B-	
722.7m, A-	CBr
723.2m, A-	CBr
870.7vw, A+B-	
871.6vw, A+B-	
955.5w, A-	C^{81}Br^+
957.0w, A-	C^{79}Br^+
1608.2vw, A+B-	
1819.4wm, B-	
1863.0m, A-	$\text{Br}^{13}\text{CN}^+ \nu_1$
1883.5wm, A-	$\text{BrC}^{15}\text{N}^+ \nu_1$
1907.7vs, A-	$\text{BrCN}^+ \nu_1$
2043.6wm, B+	CN
2044.2sh, B+	CN
2047.3m, B+	CN
2048.6vw, A+B-	
2072.2vs, B-	BrNC
2075.3m, A-	
2087.2wm, A-	
3790.5ms, A-	$\text{BrCN}^+ 2\nu_1$

removed for the second period of irradiation. Several other experiments employed a wide variety of cutoff filters during tungsten-lamp and mercury-arc irradiation of the deposit. However, no marked changes analogous to those observed in the Ne:ClCN experiments occurred. A search was also conducted for absorption bands between 4000 and 8500 cm^{-1} , but none were found.

Gas-phase studies have established that at energies between 16.6 and 16.85 eV, BrCN^+ and possibly some fragment ions may be produced from BrCN. The photoionization study by Dibeler and Liston¹⁹ yielded a first ionization energy of 11.84(1) eV for BrCN. Early photoelectron studies^{5,6}

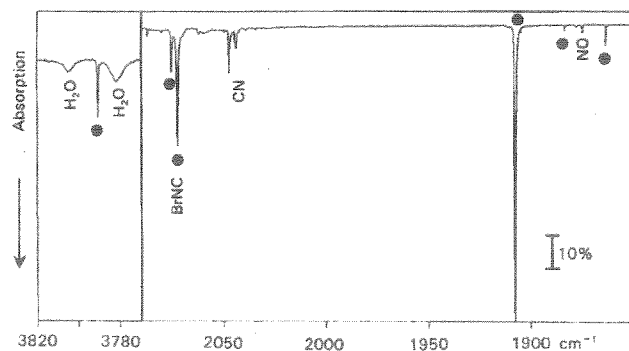


FIG. 4. New absorptions which appear in discharge sampling experiments on BrCN. 10.7 mmol Ne:BrCN=800:1 codeposited at 4.3 K over a period of 207 min with 11.0 mmol Ne that had been passed through a microwave discharge. (●) Decreases in intensity on unfiltered mercury-arc irradiation.

gave similar values. Dibeler and Liston also found an appearance energy of 15.52(2) eV for Br^+ , implying that CN and Br^+ would not be produced by excitation of ground-state BrCN^+ at energies below 3.68 eV ($29\,700 \text{ cm}^{-1}$ or 337 nm). However, they could not establish precise appearance energies of other fragment ions, which were generally above 17 eV. On this basis, these other fragment ions should not arise from irradiation of BrCN^+ at wavelengths longer than approximately 240 nm. The earlier electron impact study by Herron and Dibeler²⁰ found the appearance energy of CBr^+ from BrCN to be 17.4(2) eV. In contrast, Ibuki *et al.*³⁴ observed the onset of CBr^+ production near 20.5 eV. The infrared and electronic spectra of CBr^+ have not been reported. However, calculations at the CCSD(T)/6-311++G(3df-3pd) level by Li and Francisco³⁵ gave a value of 968 cm^{-1} for the ground-state vibrational fundamental of CBr^+ . Weak absorptions which appeared at 955.5 and 957.0 cm^{-1} in the present neon-matrix study are tentatively assigned to CBr^+ , probably produced by the ionization of initially formed CBr.

Experiments have provided considerable information regarding the energy levels of ground-state BrCN^+ in the gas phase. The early fluorescence studies of Allan and Maier⁷ and of Eland *et al.*⁸ established that the spin splitting of ground-state BrCN^+ equals $-1477(2) \text{ cm}^{-1}$. Salud *et al.*³⁶ conducted a high resolution diode laser study which found the band center for the CN-stretching fundamental, ν_1 , at 1905.95 cm^{-1} . This value is consistent with the less precise values which resulted from the fluorescence^{26,37} and high resolution photoelectron³⁸ studies. Those studies also found a value for the CBr-stretching fundamental, ν_3 , of $649.4(5) \text{ cm}^{-1}$, and the fluorescence observations yielded a value of $287.2(2) \text{ cm}^{-1}$ for the bending fundamental, ν_2 . Although a peak was attributed by Fulara *et al.*²⁶ to a transition from the band origin of the \bar{B} state of BrCN^+ to the $2\nu_1$ level of the ground-state cation, its counterpart was not identified in the reanalysis by Hanratty *et al.*³⁷ The progression in ν_1 reported by Eland *et al.* for the first photoelectron band of BrCN included a peak assigned to $2\nu_1$ at $3792(10) \text{ cm}^{-1}$.

In the present neon-matrix studies, the very strong absorption at 1907.7 cm^{-1} lies less than 2 cm^{-1} above the band center for ν_1 of gas-phase BrCN^+ . The correspondence of these two peaks is reinforced by the measurement by Ibuki *et al.*³⁴ of an ionization efficiency of 90% for BrCN at 16.5 eV. If the CN-stretching vibration of BrCN^+ is approximately separable from the two lower frequency fundamental vibrations, the position of the CN-stretching fundamental of $\text{Br}^{13}\text{CN}^+$ present in natural abundance can be estimated using the familiar diatomic molecule relationship. The resulting value is 1867.8 cm^{-1} . A moderately intense absorption which has the same photodestruction behavior as the carrier of the 1907.7 cm^{-1} absorption appears at 1863.0 cm^{-1} . Similarly, the position of the CN-stretching fundamental of $\text{BrC}^{15}\text{N}^+$ is estimated to be 1878.1 cm^{-1} , and a weak to moderately intense absorption with similar photodestruction behavior appears at 1883.5 cm^{-1} . The absorption at 3790.5 cm^{-1} lies at the appropriate position for $2\nu_1$ of BrCN^+ .

Recently, Biczysko and Tarroni¹⁹ reported results of a

theoretical study of the coupling of Renner-Teller interactions to large spin-orbit splittings, as illustrated by BrCN⁺. This study included high-level *ab initio* calculations of vibronic energy levels of Σ , Π , Δ , and Φ symmetries from 0 to 9000 cm⁻¹. For the lower spin-orbit component of the ground state, the calculated positions of the three fundamentals are 1912.5, 279.8 ($\mu\Sigma$ level), and 650.3 cm⁻¹, in excellent agreement with the gas-phase values. These workers obtained a value of 3802.2 cm⁻¹ for $2\nu_1$ of BrCN⁺, in very good agreement with both the high resolution photoelectron measurements³⁸ and the present neon-matrix assignment. The many other combination and overtone bands calculated by Biczysko and Tarroni were not detected in the present experiments, presumably because their infrared absorptions are relatively weak.

D. Electron attachment to ClCN and BrCN

Earlier studies provide scant evidence for the stabilization of ClCN⁻ and BrCN⁻. Brüning *et al.*⁴⁰ conducted a crossed-beam study of electron attachment to ClCN and BrCN. For both molecules the predominant anion was CN⁻, which had a prominent maximum at electron energies near 0 eV. The X⁻ signal was much smaller, with its maximum somewhat above 0 eV. The XCN⁻ signal had a maximum at 0 eV but was two or three orders of magnitude weaker than the CN⁻ signal. Very recent *ab initio* calculations by Royal and Orel⁴¹ of the dissociative attachment cross sections of electrons to these two molecules were consistent with the observations of Brüning *et al.* but yielded positions of the prominent maxima for CN⁻ production at 0.62 eV for ClCN and at 0.42 eV for BrCN.

There is evidence for the stabilization of CN⁻ in at least the Ne:ClCN experiments. Forney *et al.*¹⁰ assigned the infrared absorption which appears at 2053.1 cm⁻¹ in the analogous Ne:HCN experiments to CN⁻. The 2054.0 cm⁻¹ peak in the Ne:ClCN experiments is sufficiently close to suggest its assignment to CN⁻, which may be slightly perturbed by the presence of ClCN in nearby sites. The electron affinity of CN is unusually large, 3.862(4) eV.⁴² This value corresponds to a gas-phase photodetachment threshold of 321 nm. The photodetachment of anions trapped in solid neon generally requires photon energies that exceed the photodetachment threshold by 1 or 2 eV, in order to impart sufficient kinetic energy to the electron for it to avoid reattachment. If most of the anions in the Ne:ClCN deposit are CN⁻, photoisomerization of ClCN⁺ to CINC⁺ using radiation of wavelength longer than 345 nm should not degrade the concentration of ions in the sample, consistent with the observations.

IV. CONCLUSIONS

On excitation of XCN (X=Cl,Br) at energies between 16.6 and 16.85 eV, followed by rapid quenching of the products in solid neon at 4.3 K, prominent infrared absorptions result from both photoisomerization and photoionization of the XCN. The NC-stretching absorptions of CINC and BrNC isolated in solid neon lie close to their previously reported argon-matrix counterparts. The CN-stretching absorptions of ClCN⁺ and BrCN⁺ and the CCl-stretching absorption of

ClCN⁺ lie very close to the gas-phase band centers. In the studies on ClCN, absorptions contributed by one overtone and one combination band of ClCN⁺ also appear. In addition, an absorption at 642.8 cm⁻¹ probably is contributed by the lower energy Π component of $2\nu_2$ of ground-state ClCN⁺. Reversible photoisomerization of ClCN⁺ to form CINC⁺ occurs. The two stretching vibrational fundamentals of CINC⁺ are identified, and several broad infrared and near infrared absorptions are attributed to one or more electronic transitions of CINC⁺. No evidence was obtained for the photoisomerization of BrCN⁺.

- ¹D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47**, 278 (1967).
- ²M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **48**, 4040 (1968).
- ³T. J. Lee and S. C. Racine, *Mol. Phys.* **84**, 717 (1995).
- ⁴T. J. Lee, J. M. L. Martin, C. E. Dateo, and P. R. Taylor, *J. Phys. Chem.* **99**, 15858 (1995).
- ⁵E. Heilbronner, V. Hornung, and K. A. Muszkat, *Helv. Chim. Acta* **53**, 347 (1970).
- ⁶R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A* **317**, 187 (1970).
- ⁷M. Allan and J. P. Maier, *Chem. Phys. Lett.* **41**, 231 (1976).
- ⁸J. H. D. Eland, M. Devoret, and S. Leach, *Chem. Phys. Lett.* **43**, 97 (1976).
- ⁹M. E. Jacox, *Chem. Soc. Rev.* **31**, 108 (2002).
- ¹⁰D. Forney, W. E. Thompson, and M. E. Jacox, *J. Chem. Phys.* **97**, 1664 (1992).
- ¹¹M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **126**, 054308 (2007).
- ¹²Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.
- ¹³M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **91**, 1410 (1989).
- ¹⁴M. E. Jacox and W. B. Olson, *J. Chem. Phys.* **86**, 3134 (1987).
- ¹⁵R. A. Toth, *J. Opt. Soc. Am. B* **8**, 2236 (1991); **10**, 2006 (1993).
- ¹⁶F. Stroh and M. Winnewisser, *Chem. Phys. Lett.* **155**, 21 (1989); F. Stroh, B. P. Winnewisser, M. Winnewisser, H. P. Reisenauer, G. Maier, S. J. Goede, and F. Bickelhaupt, *ibid.* **160**, 105 (1989); **162**, 253 (1989).
- ¹⁷C. Yamada, K. Nagai, and E. Hirota, *J. Mol. Spectrosc.* **85**, 416 (1981).
- ¹⁸D. Forney, M. E. Jacox, and W. E. Thompson, *J. Mol. Spectrosc.* **157**, 479 (1993).
- ¹⁹V. H. Dibeler and S. K. Liston, *J. Chem. Phys.* **47**, 4548 (1967).
- ²⁰J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.* **82**, 1555 (1960).
- ²¹H. Bredohl, I. Dubois, and F. Melen, *J. Mol. Spectrosc.* **98**, 495 (1983).
- ²²K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules, Molecular Spectra and Molecular Structure Vol. 4* (Van Nostrand, New York, 1979).
- ²³D.-C. Wang, F. T. Chau, E. P. F. Lee, A. K.-M. Leung, and J. M. Dyke, *Mol. Phys.* **93**, 995 (1998).
- ²⁴S. Mishra, V. Vallet, L. V. Poluyanov, and W. Domcke, *J. Chem. Phys.* **124**, 044317 (2006).
- ²⁵S. Leutwyler, J. P. Maier, and U. Spittel, *J. Chem. Phys.* **83**, 506 (1985).
- ²⁶J. Fulara, D. Klapstein, R. Kuhn, and J. P. Maier, *J. Phys. Chem.* **89**, 4213 (1985).
- ²⁷F. J. Greiman, A. McIlroy, and J. Perkins, *J. Chem. Phys.* **84**, 2481 (1986).
- ²⁸D. M. P. Holland, D. A. Shaw, L. Karlsson, L. G. Shpinkova, L. Cooper, A. B. Trofimov, and J. Schirmer, *Mol. Phys.* **98**, 1939 (2000).
- ²⁹F. G. Celii, J. Fulara, J. P. Maier, and M. Rösslein, *Chem. Phys. Lett.* **131**, 325 (1986).
- ³⁰F. G. Celii, M. Rösslein, M. A. Hanratty, and J. P. Maier, *Mol. Phys.* **62**, 1435 (1987); M. Rösslein and J. P. Maier, *J. Phys. Chem.* **93**, 7342 (1989).
- ³¹J. P. Maier, M. Ochsner, and F. Thommen, *Faraday Discuss. Chem. Soc.* **75**, 77 (1983).
- ³²O. Braithbart, E. Castellucci, G. Dujardin, and S. Leach, *J. Phys. Chem.* **89**, 3252 (1985).
- ³³A. J. Marr, T. J. Sears, and P. B. Davies, *J. Mol. Spectrosc.* **184**, 413 (1997).

- ³⁴T. Ibuki, A. Hiraya, T. N. Olney, and C. E. Brion, *Chem. Phys.* **203**, 359 (1996).
- ³⁵Z. Li and J. S. Francisco, *J. Chem. Phys.* **109**, 134 (1998).
- ³⁶C. Salud, M. Fehér, and T. Amano, *J. Mol. Spectrosc.* **162**, 172 (1993).
- ³⁷M. A. Hanratty, M. Rösslein, F. G. Celli, T. Wytttenbach, and J. P. Maier, *Mol. Phys.* **64**, 865 (1988).
- ³⁸J. H. D. Eland, P. Baltzer, M. Lundqvist, B. Wannberg, and L. Karlsson, *Chem. Phys.* **212**, 457 (1996).
- ³⁹M. Biczysko and R. Tarroni, *Chem. Phys. Lett.* **415**, 223 (2005).
- ⁴⁰F. Brüning, I. Hahndorf, A. Stamatovic, and E. Illenberger, *J. Phys. Chem.* **100**, 19740 (1996).
- ⁴¹J. Royal and A. E. Orel, *J. Chem. Phys.* **125**, 214307 (2006).
- ⁴²S. E. Bradforth, E. H. Kim, D. W. Arnold, and D. M. Neumark, *J. Chem. Phys.* **98**, 800 (1993).