

Infrared signatures of the NCCO radical

Peter R. Schreiner,^{*a} Hans Peter Reisenauer,^a Edit Mátyus,^b Attila G. Császár,^{*b}
Ali Siddiqi,^c Andrew C. Simmonett^c and Wesley D. Allen^{*c}

Received 29th June 2009, Accepted 11th August 2009

First published as an Advance Article on the web 28th September 2009

DOI: 10.1039/b912803d

The first definitive infrared signatures of the elusive NCCO radical have been measured using a microwave discharge technique combined with low-temperature matrix-isolation spectroscopy, resulting in a consistent set of vibrational assignments for six isotopologues. The infrared spectra of these NCCO isotopologues were concomitantly established by rigorous variational nuclear-motion computations based on a high-level coupled-cluster quartic vibrational force field [ROCCSD(T)/cc-pCVQZ] and cubic dipole field [ROCCSD/cc-pCVTZ]. Our experimental and theoretical results for NCCO overturn the vibrational assignments in a NIST-JANAF compilation and those from a recent two-dimensional cross-spectral correlation analysis. For the parent isotopologue at 11 K in a nitrogen matrix, we find the signature bands $\nu_2(\text{CO str.}) = 1889.2 \text{ cm}^{-1}$ and $\nu_3(\text{CC str.}) = 782.0 \text{ cm}^{-1}$. Our variational vibrational computations reveal strong mixing of the ν_3 stretching fundamental and the $\nu_4 + \nu_5$ bending combination level for all isotopologues. These Fermi resonances manifest a clear breakdown of the simple normal-mode picture of molecular vibrations at low energies.

1. Introduction

Although the NCCO (carbonyl cyanide) radical may play a significant role in combustion chemistry,¹ reliable infrared (IR) signatures of this species have proved elusive,^{2,3} and the molecule remains poorly characterized. Proposed experimental assignments⁴ of the most intense infrared absorptions of NCCO, corresponding to the CN ($\nu_1 = 2093 \text{ cm}^{-1}$) and CO ($\nu_2 = 1774 \text{ cm}^{-1}$) stretching fundamentals, are in severe disagreement with recent state-of-the-art *ab initio* predictions [$\nu_1(\omega_1) = 2171(2214) \text{ cm}^{-1}$; $\nu_2(\omega_2) = 1898(1919) \text{ cm}^{-1}$] based on a high-level coupled-cluster [AE-ROCCSD(T)/cc-pCVQZ] anharmonic force field and second-order vibrational perturbation theory (VPT2).³ Confusion over the IR vibrational band origins (VBOs) is compounded by earlier quadratic configuration interaction [QCISD(T)/6-31G(d)] computations that gave harmonic frequencies of $\omega_1 = 2304 \text{ cm}^{-1}$ and $\omega_2 = 1936 \text{ cm}^{-1}$ for the key stretching vibrations.⁵

Among several theoretical studies,^{3,5-9} the best existing work³ [AE-ROCCSD(T)/cc-pCVQZ] for NCCO has found a *trans*-bent ${}^2A'$ ground electronic state of C_s symmetry with N–C–C and C–C–O equilibrium angles of 168.6° and 132.2° , respectively. The $\tilde{A}{}^2A''$ excited state of NCCO collapses to linearity upon geometry optimization³ and coalesces with the $\tilde{X}{}^2A'$ state to form a case (C) Renner–Teller system¹⁰ of ${}^2\Pi$ symmetry. The electronic structure of NCCO is thus

analogous to that of HCO,¹¹ suggesting that carbonyl cyanide can be considered a derivative of the formyl radical involving substitution with the pseudohalogen CN. Nonetheless, NCCO($\tilde{X}{}^2A'$) has a computed barrier to linearity ($8.4 \text{ kcal mol}^{-1}$)³ and C–C–O angle (132.2°) considerably different from the corresponding HCO experimental values of $26.6 \text{ kcal mol}^{-1}$ and $\angle\text{H–C–O} = 124.4^\circ$, respectively.^{11,12} The *ab initio* limit for the NCCO \rightarrow CN + CO dissociation energy is $D_0 = 26.5 \text{ kcal mol}^{-1}$,³ a remarkably small carbon–carbon bond energy roughly twice the minuscule $D_0 = 14.4 \text{ kcal mol}^{-1}$ established for the HCO \rightarrow H + CO analogue.¹³

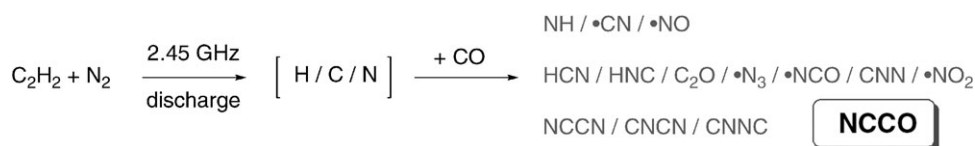
The preparation of NCCO from a variety of precursors has been documented by mass spectrometric detection.^{4,14} The NCCO radical is the major photolysis product of methyl cyanoformate [NCC(O)OCH₃], carbonyl cyanide [CO(CN)₂], and pivaloyl cyanide [NCC(O)C(CH₃)₃] at 193 nm, whereas acetyl cyanide [CH₃C(O)CN] yields NCCO in lower abundance than CN at the same wavelength.¹⁵⁻¹⁹ However, very recent photolysis studies on CO(CN)₂ in cryogenic matrices failed to identify the expected NCCO radical by IR spectroscopy.¹⁸ The difficulty in isolating NCCO after photochemical generation is that the nascent product may decompose by further ultraviolet (UV) absorptions in the same region. Therefore, we have pursued the preparation of NCCO by thermal means.

In 1992, experiments performed in one of our laboratories²⁰ showed that cyano radicals formed in a plasma generated by a microwave discharge in a stream of acetylene doped with nitrogen could be frozen out at 10 K on the surface of a spectroscopic window. Fourier-transform infrared (FTIR) and ultraviolet-visible (UV/VIS) spectra of the matrices formed in this manner revealed the presence of not only monomeric CN radicals but also the three possible dimers NC–CN (cyanogen), NC–NC (isocyanogen) and CN–NC (diisocyanogen). The identification of the dimeric species was

^a Institut für Organische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.
E-mail: prs@org.chemie.uni-giessen.de

^b Laboratory of Molecular Spectroscopy, Institute of Chemistry, Eötvös University, H-1518 Budapest 112, P.O. Box 32 Hungary.
E-mail: esaszar@chem.elte.hu

^c Center for Computational Chemistry and Department of Chemistry, University of Georgia, Athens, GA 30602, USA.
E-mail: wdallen@uga.edu



Scheme 1 Generation of NCCO by decomposition of N₂ and acetylene followed by recombination in the presence of CO.

established by extensive isotopic substitution using ¹⁵N₂ and ¹³C₂H₂ as starting materials. The observation of additional products, such as NH₃, NH₂, NH, HCN, and HNC, as well as small amounts of CO, NO, NCO, N₃, and HCO, suggests that in the plasma all starting materials are broken down to the atomic level and are then re-assembled en route to or within the matrix.

With the goal of producing matrix-isolated NCCO radicals, we have extended the microwave discharge technique by co-condensing on a cold window a separate stream of carbon monoxide with the products from the plasma generated in the acetylene–nitrogen stream, anticipating reactions of CN radicals with CO during formation of the matrix (Scheme 1). The experimental studies reported here combined with decisive quantum chemical computations provide definitive infrared signatures of the elusive NCCO radical and demonstrate that earlier experimental vibrational assignments are in error.

2. Methods

2.1 Experimental

In a typical experiment, a gaseous mixture of 0.5% acetylene or 0.5% cyanogen in N₂ flowed through a quartz tube (*ca.* 10 × 200 mm) in which a discharge was maintained by a 2.45 GHz microwave generator (Fig. 1). Immediately after leaving the plasma zone, the gaseous stream was frozen at 11 K on the spectroscopic window of the cryostat. Pure CO was added simultaneously through a separate inlet capillary and co-condensed on the spectroscopic window. The nitrogen matrix thus formed was examined by FTIR spectroscopy in the spectral range 400–4500 cm⁻¹ with a resolution of 0.7 cm⁻¹ directly after condensation and also after heating the matrix to 27 and 30 K for *ca.* 10 min and re-cooling to 11 K. By conducting experiments with combinations of ¹⁵N₂ and ¹³C₂H₂ with ¹²CO and ¹³CO, band positions were measured for the following six isotopologues of the carbonyl cyanide radical: ¹⁴N¹²C¹²C¹⁶O, ¹⁵N¹²C¹²C¹⁶O, ¹⁴N¹²C¹³C¹⁶O, ¹⁴N¹³C¹²C¹⁶O, ¹⁵N¹²C¹³C¹⁶O, and ¹⁴N¹³C¹³C¹⁶O. The matrix-isolation vibrational frequencies are expected to be shifted by about 0.2% from the corresponding gas-phase values.²¹

The cryostat used for the matrix-isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF₂ windows for UV/VIS measurements. IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer. The discharge experiments utilized a Ratheon Microwave power generator (model PGM 10X1) with a cavity E14c.

2.2 Computational

The complete quartic vibrational force field of NCCO (\tilde{X}^2A') was computed in an internal-coordinate representation in

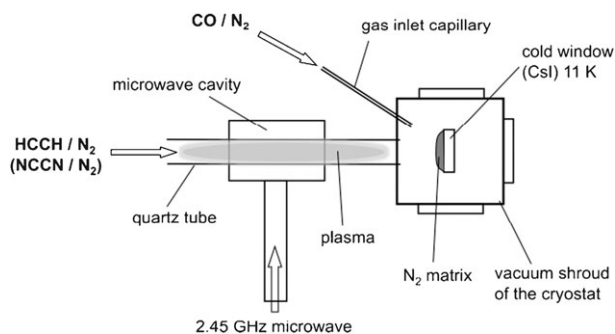


Fig. 1 Experimental setup used to generate NCCO and trap it in an N₂ matrix on a cold window.

recent work³ by some of us that utilized all-electron (AE) ROCCSD(T) restricted open-shell coupled-cluster theory^{22–24} with a large correlation-consistent polarized core-valence quadruple-zeta (cc-pCVQZ) basis set containing an [8s7p5d3/1g] collection of functions for each atom.²⁵ In the current study, this high-accuracy AE-ROCCSD(T)/cc-pCVQZ force field was transformed into Simons–Parr–Finlan bond-stretching coordinates²⁶ using the INTDER program^{27–30} and then employed in our variational vibrational computations. The equilibrium reference structure for this force field is $r_e(\text{N–C}) = 1.1623 \text{ \AA}$, $r_e(\text{C–C}) = 1.4370 \text{ \AA}$, $r_e(\text{C–O}) = 1.1758 \text{ \AA}$, $\theta_e(\text{N–C–C}) = 168.55^\circ$, and $\theta_e(\text{C–C–O}) = 132.22^\circ$.

To determine infrared vibrational intensities, an internal-coordinate cubic dipole field of NCCO was computed in this study using the all-electron ROCCSD restricted open-shell coupled-cluster singles and doubles method^{31–34} conjoined with a cc-pCVTZ basis set of [6s5p3d1f] quality for each atom.²⁵ The AE-ROCCSD/cc-pCVTZ dipole moments were evaluated as energy derivatives with respect to external electric fields *via* analytic gradient techniques within the PSI3 package.³⁵ High-order central difference formulae were employed to determine the complete cubic dipole field from dipole moments computed on a grid of 125 geometric structures, as carried out by the INTDIF program.^{36,37} The AE-ROCCSD(T)/cc-pCVQZ equilibrium geometry was chosen as the reference structure for computing the AE-ROCCSD/cc-pCVTZ dipole field, thus averting ambiguities in defining the body-fixed axes. The cubic dipole field was first computed for the parent isotopologue (¹⁴N¹²C¹²C¹⁶O) using geometric displacements supplied by INTDER to satisfy the Eckart conditions.^{38,39} Internal-coordinate dipole fields for each of the other isotopologues were then obtained by rotating the dipole moments for the ¹⁴N¹²C¹²C¹⁶O displacements to the appropriate Eckart body-fixed axis system and then applying the numerical differentiation formulae again.

Converged variational vibrational energy levels and wave functions for ¹⁴N¹²C¹²C¹⁶O, ¹⁵N¹²C¹²C¹⁶O, ¹⁴N¹²C¹³C¹⁶O,

$^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$, $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$, and $^{14}\text{N}^{13}\text{C}^{13}\text{C}^{16}\text{O}$ were computed by the DEWE program system.^{40,41} DEWE is based on the discrete variable representation (DVR)^{42–44} of the Watson Hamiltonian⁴⁵ and allows the exact inclusion of a potential energy surface (PES) represented in arbitrarily chosen coordinates. For comparison, auxiliary results were obtained by means of conventional second-order vibrational perturbation theory (VPT2).^{46–48}

The DEWE computations employed a direct product Hermite-DVR grid, having 9 grid points for each vibrational degree of freedom. Such a grid provides convergence to within 0.1 cm^{-1} for the fundamentals, as well as the combination and overtone levels strongly mixing with the fundamentals. The atomic masses (in u) adopted in the computations were $m(^{14}\text{N}) = 14.003074$, $m(^{15}\text{N}) = 15.000109$, $m(^{12}\text{C}) = 12$, $m(^{13}\text{C}) = 13.003355$, and $m(^{16}\text{O}) = 15.994915$.

The numerically exact variational vibrational wave functions, ψ_i , provided by DEWE were characterized by their overlap with the multidimensional harmonic oscillator basis states, ϕ_j , from the normal-mode approximation. The overlap coefficients are organized into a matrix,

$$\text{NMD}[i,j] = \langle \psi_i | \phi_j \rangle^2,$$

which provides the normal-mode decomposition (NMD) of the full variational wave function, thus facilitating quantitative vibrational assignments.

Absolute integrated infrared band intensities (A) were computed by evaluating transition matrix elements of the dipole field over the variational vibrational wave functions. The working formula³⁸ implemented within DEWE, appropriate for low temperatures, is

$$A(\tilde{\nu}_f \leftarrow \tilde{\nu}_0)/(\text{km mol}^{-1}) = 2.506562213[(\tilde{\nu}_f - \tilde{\nu}_0)/\text{cm}^{-1}] \sum_{\alpha=x,y,z} [|\langle \psi_f | \mu_\alpha | \psi_0 \rangle|^2 / \text{Debye}^2]$$

where $(0,f)$ denote (ground, final) states with vibrational energies $(\tilde{\nu}_0, \tilde{\nu}_f)$ and wave functions (ψ_0, ψ_f) , and the dipole vector is expressed in the body-fixed axis system (x,y,z) .

3. Results and discussion

The plasma reactions within the $\text{C}_2\text{H}_2/\text{N}_2$ (or NCCN/N_2) streams generated a complex mixture of two, three, and four-atomic species that could be identified using known band positions²⁰ from FTIR spectra of the matrix formed without the additional stream of CO. The formation of the numerous products can be understood by assuming complete atomization of the precursor molecules in the plasma with subsequent recombination. Co-condensation with the CO stream caused the appearance of additional IR bands in the matrix, from which NCCO can be identified. Although these IR spectra are rich in signals from various other species (Scheme 1), intense absorptions attributable to NCCO can be readily singled out, as shown in Fig. 2. The preparation of six isotopologues of NCCO solidified our IR assignments by the measurement of characteristic isotopic shifts (Fig. 3), which are in remarkable accord with our high-level *ab initio* anharmonic vibrational computations. The theoretical and experimental vibrational

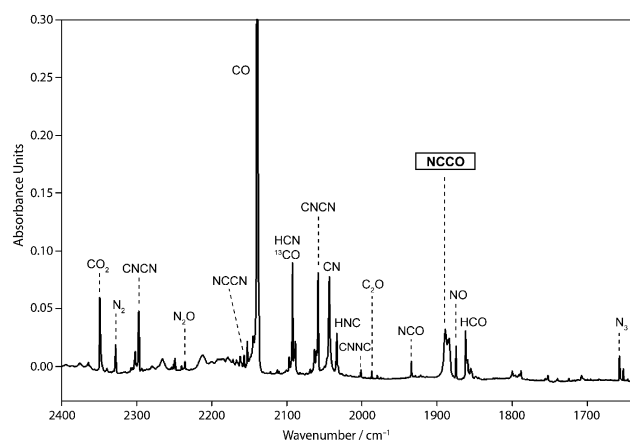


Fig. 2 “Raw” IR matrix-isolation spectrum (excess N_2 as matrix material, 11 K) of all species generated *via* Scheme 1.

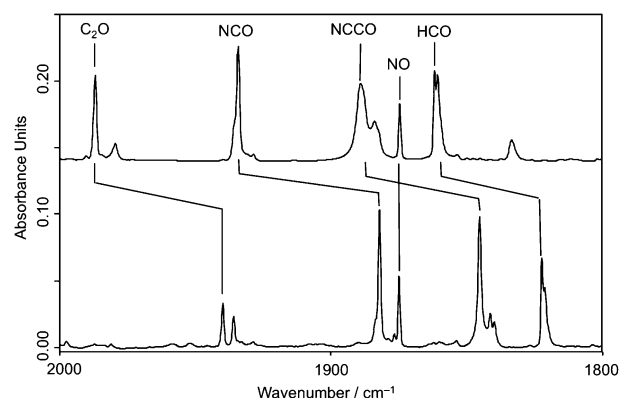


Fig. 3 Part of the FTIR spectrum of the matrix-isolated products of discharged gaseous mixture (N_2 , 0.5% cyanogen) and co-condensed $^{12}\text{C}^{16}\text{O}$ (upper trace) and $^{13}\text{C}^{16}\text{O}$ (lower trace) at 15 K showing the specific isotopic shifts. Upper trace: $^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$, lower: $^{14}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$.

band origins and isotopic shifts obtained in this study for NCCO isotopologues are collected in Table 1, along with computed infrared intensity and normal-mode decomposition data.

3.1 The ν_2 fundamental

When $^{12}\text{C}^{16}\text{O}$ is co-condensed with the microwave discharge products of $^{14}\text{N}_2/^{12}\text{C}_2\text{H}_2$, the resulting FTIR matrix-isolation spectra show strongly enhanced bands at 1987.2 cm^{-1} (C_2O , reaction with a carbon atom), 1934.5 cm^{-1} (NCO, reaction with a nitrogen atom), 1822.1 cm^{-1} (HCO, reaction with a hydrogen atom), and 1889.2 cm^{-1} . The latter band very closely matches the $\nu_2(\text{CO str.})$ fundamental for the parent NCCO radical predicted at 1897.8 cm^{-1} by the variational computations. For the five substituted NCCO isotopologues, similar enhanced FTIR bands appear in the $1840\text{--}1890\text{ cm}^{-1}$ range which are also within $7\text{--}9\text{ cm}^{-1}$ of the corresponding theoretical $\nu_2(\text{CO str.})$ fundamentals. For all six isotopologues studied here, the variationally computed $\nu_2(\text{CO str.})$ absorptions are very strong ($103\text{--}135\text{ km mol}^{-1}$) and more intense than the other NCCO bands by at least a factor of 6. The striking match between the experimental and

Table 1 Experimental and theoretical vibrational fundamentals (cm^{-1}) for six NCCO isotopologues. Isotopic shifts (cm^{-1}) relative to the parent $^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$ are listed in parentheses; computed absolute infrared intensities from the cubic (linear) dipole fields are given in km mol^{-1} . VPT2 = second-order vibrational perturbation theory; DEWE = variational nuclear-motion results; NMD = normal-mode decomposition

Mode	Method	$^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$	$^{15}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$	$^{14}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$	$^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$	$^{15}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$	$^{14}\text{N}^{13}\text{C}^{13}\text{C}^{16}\text{O}$
ν_1 (a') CN stretch	DEWE	2171.2 (0)	2145.0 (−26.2)	2170.1 (−1.1)	2126.7 (−44.5)	2141.8 (−29.4)	2121.0 (−50.2)
	VPT2	2171.0 (0)	2143.6 (−27.4)	2170.1 (−0.9)	2123.1 (−47.9)	2142.1 (−28.9)	2120.9 (−50.1)
	Intensity	21 (19)	24 (22)	19 (18)	21 (16)	12 (12)	17 (16)
	NMD	$0.84\nu_1$	$0.84\nu_1$	$0.92\nu_1$	$0.61\nu_1 + 0.27(\nu_5 + \nu_2)$	$0.55\nu_1$	$0.81\nu_1$
ν_2 (a') CO stretch	Experiment	1889.2 (0)	1888.2 (−1.0)	1845.1 (−44.1)	1889.2 (0.0)	1844.2 (−45.0)	1845.2 (−44.0)
	DEWE	1897.8 (0)	1896.6 (−1.2)	1852.7 (−45.1)	1896.3 (−1.5)	1851.3 (−46.5)	1854.4 (−43.4)
	VPT2	1898.0 (0)	1897.2 (−0.8)	1854.5 (−43.5)	1897.7 (−0.3)	1853.9 (−44.1)	1854.3 (−43.7)
	Intensity	128 (124)	135 (131)	126 (122)	132 (129)	103 (100)	114 (111)
	NMD	$0.85\nu_2$	$0.90\nu_2$	$0.87\nu_2$	$0.88\nu_2$	$0.71\nu_2$	$0.80\nu_2$
ν_3 (a') CC stretch	Experiment	782.0 (0)	777.1 (−4.9)	769.5 (−12.5)	775.2 (−6.8)	763.8 (−18.2)	762.9 (−19.1)
	DEWE	786.1 (0)	781.1 (−5.0)	775.0 (−11.1)	776.8 (−9.3)	769.4 (−16.7)	766.6 (−19.5)
	VPT2	797.5 (0)	791.8 (−5.7) ^a	774.1 (−23.4) ^a	790.8 (−6.7) ^a	791.7 (−5.3) ^a	770.9 (−26.1) ^a
	Intensity	7 (10)	8 (11)	10 (13)	4 (7)	11 (13)	8 (11)
	NMD	$0.49\nu_3 + 0.38(\nu_4 + \nu_5)$	$0.53\nu_3 + 0.35(\nu_4 + \nu_5)$	$0.65\nu_3 + 0.18(\nu_4 + \nu_5)$	$0.53(\nu_4 + \nu_5) + 0.36\nu_3$	$0.69\nu_3 + 0.16(\nu_4 + \nu_5)$	$0.55\nu_3 + 0.32(\nu_4 + \nu_5)$
	DEWE'	803.3 (0)	798.0 (−5.3)	793.5 (−9.9)	795.2 (−8.1)	788.6 (−14.8)	784.0 (−19.3)
	Intensity'	12 (8)	11 (7)	8 (4)	14 (11)	7 (3)	10 (6)
	NMD'	$0.51(\nu_4 + \nu_5) + 0.41\nu_3$	$0.55(\nu_4 + \nu_5) + 0.37\nu_3$	$0.69(\nu_4 + \nu_5) + 0.22\nu_3$	$0.55\nu_3 + 0.37(\nu_4 + \nu_5)$	$0.73(\nu_4 + \nu_5) + 0.19\nu_3$	$0.57(\nu_4 + \nu_5) + 0.35\nu_3$
ν_4 (a') Sym in-plane Bend	DEWE	576.1 (0)	573.4 (−2.8)	571.4 (−4.7)	567.1 (−9.0)	568.8 (−7.3)	562.2 (−13.9)
	VPT2	577.0 (0)	574.0 (−3.0)	572.7 (−4.3)	568.4 (−8.6)	570.1 (−6.9)	563.5 (−13.5)
	Intensity	2 (2)	1 (2)	2 (3)	2 (2)	2 (2)	2 (2)
	NMD	$0.95\nu_4$	$0.95\nu_4$	$0.95\nu_4$	$0.95\nu_4$	$0.95\nu_4$	$0.95\nu_4$
ν_5 (a') Asym in-plane Bend	DEWE	221.8 (0)	219.8 (−1.9)	220.0 (−1.7)	219.1 (−2.6)	218.1 (−3.6)	217.5 (−4.2)
	VPT2	221.8 (0)	219.9 (−1.9)	220.1 (−1.7)	219.2 (−2.6)	218.2 (−3.6)	217.6 (−4.2)
	Intensity	10 (10)	9 (10)	9 (10)	9 (10)	9 (10)	9 (10)
	NMD	$0.96\nu_5$	$0.96\nu_5$	$0.96\nu_5$	$0.96\nu_5$	$0.96\nu_5$	$0.96\nu_5$
ν_6 (a'') Out-of-plane Bend	DEWE	269.6 (0)	267.7 (−2.0)	269.0 (−0.6)	262.3 (−7.3)	267.0 (−2.6)	261.7 (−8.0)
	VPT2	269.6 (0)	267.6 (−2.0)	269.0 (−0.6)	262.3 (−7.3)	267.0 (−2.6)	261.7 (−7.9)
	Intensity	11 (10)	10 (10)	10 (11)	10 (10)	10 (10)	10 (10)
	NMD	$0.96\nu_6$	$0.96\nu_6$	$0.96\nu_6$	$0.96\nu_6$	$0.96\nu_6$	$0.96\nu_6$

^a Treatment of the ($\nu_3, \nu_4 + \nu_5$) resonance in first rather than second order yields isotopic shifts of −5.9, −19.8, −6.4, −25.0, and −19.6 cm^{-1} for the NCCO isotopologues, from left to right in order.³

theoretical isotopic shifts (Table 1) leaves no doubt about the infrared assignments for the ν_2 fundamental of NCCO, as the mean absolute difference between the measured and computed shifts is only 1.0 cm^{-1} .

The CO stretching fundamental of NCCO shows a broadening and splitting into at least two components and has a shape significantly different from the band contours for species such as C_2O , NCO, and NO. However, similar structure can be observed in the CO stretching band of matrix-isolated HCO. Variations of host sites are presumably responsible for the band splittings and broadenings, a phenomenon often observed in matrix-isolation spectroscopy.⁴⁹

Our observation of ν_2 of $^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$ at 1889.2 cm^{-1} is drastically different from the $\nu_2 = 1774 \text{ cm}^{-1}$ result of McNavage and Dai.⁴ In their rather convoluted experiments, carbonyl cyanide, pivaloyl cyanide, and methyl cyanofornate were photolyzed, the products were probed by time-resolved Fourier-transform infrared emission spectroscopy, and the signals were disentangled by two-dimensional cross-spectra correlation analysis. By comparison, our matrix-isolation experiments are more direct, and our assignments are confirmed by definitive *ab initio* computations that invoke

no empirical scale factors. The ν_2 frequency of NCCO measured here is substantially higher than a typical carbonyl stretching frequency (*ca.* 1715 cm^{-1}) but less than the corresponding values in NCO (1921 cm^{-1}),⁵⁰ HCCO (2023 cm^{-1}),⁵¹ and H_2CCO (2153 cm^{-1}).⁵² Our $\nu_2(\text{NCCO})$ is closely matched by the observed C=O stretching frequency (1884.59 cm^{-1}) for the CICO radical,⁵³ supporting the view that the −CN group functions as a pseudohalogen in the carbonyl cyanide molecule.

3.2 The ν_3 fundamental

The variational nuclear-motion computations (Table 1) for NCCO predict that in the 760–805 cm^{-1} region there are two vibrational band origins of comparable but modest IR intensity (4–14 km mol^{-1}) arising from a ($\nu_3, \nu_4 + \nu_5$) Fermi resonance between the CC stretching fundamental and the first combination level of the in-plane bends, with concomitant intensity borrowing. For the parent isotopologue, there is a vibrational level at 786.1 cm^{-1} with the normal-mode decomposition $\text{NMD} = 0.49\nu_3 + 0.38(\nu_4 + \nu_5)$ and another level at 803.3 cm^{-1} with $\text{NMD} = 0.41\nu_3 + 0.51(\nu_4 + \nu_5)$.

While the proportions vary, this strong mixing is also observed for the other isotopologues. Except in the $^{14}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$ case, the NMD component for ν_3 is greatest in the lower vibrational level. Due to the Fermi resonance interaction, the VPT2 perturbation theory results for the $(\nu_3, \nu_4 + \nu_5)$ pair are not reliable, and one should rely only on the variational DEWE computations for these bands.

In the matrix-isolation spectrum of the $^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$ parent, a band appears at 782.0 cm^{-1} that has much lower intensity than ν_2 . We assign this absorption to the CC-stretching fundamental (ν_3) based on its excellent agreement (within 5 cm^{-1}) with the variational vibrational computation. The experimental resolution of a separate $\nu_4 + \nu_5$ band is apparently hindered by the lack of intensity in this region. For the $^{15}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$, $^{14}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$, $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{16}\text{O}$, and $^{14}\text{N}^{13}\text{C}^{13}\text{C}^{16}\text{O}$ isotopologues, bands attributable to ν_3 (CC str.) were measured at 777.1 , 769.5 , 763.8 , and 762.9 cm^{-1} , respectively. These assignments are strongly supported by the agreement between theoretical and experimental isotopic shifts to within 1.5 cm^{-1} .

The $^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$ isotopologue is the most intriguing case. The measured absorption at 775.2 cm^{-1} agrees very well with the variationally computed band origin of 776.8 cm^{-1} . However, the corresponding vibrational wave function has the normal-mode decomposition $\text{NMD} = 0.36\nu_3 + 0.53(\nu_4 + \nu_5)$, indicating that the final state has more $\nu_4 + \nu_5$ bending than ν_3 stretching character. The vibrational computations determine that the state with greatest CC-stretch contribution occurs at 795.2 cm^{-1} with $\text{NMD} = 0.55\nu_3 + 0.37(\nu_4 + \nu_5)$. If this latter state is considered the ν_3 fundamental level, then the CC stretch experiences an isotopic shift of $+9.1\text{ cm}^{-1}$ in going from the parent to $^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$, *i.e.*, a counter-intuitive blue-shift of ν_3 occurs upon substitution of one ^{12}C nucleus with a heavier ^{13}C isotope. Thus, $^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$ illustrates the intricacies that can arise in assigning a vibrational fundamental in the presence of strong mixing within a Fermi resonance pair. To avoid artificial assignments, we have evaluated the $(\nu_3, \nu_4 + \nu_5)$ isotopic shifts in Table 1 on the basis of the energetic ordering of the two states rather than the largest component of the normal-mode decomposition.

The relative infrared intensities of the two $(\nu_3, \nu_4 + \nu_5)$ mixed bands of the NCCO isotopologues are sensitive to level of theory; moreover, the experimental band profiles in this region appear to be significantly altered by matrix effects. In the variational vibrational computations, the higher-frequency band is the most intense for most isotopologues (four out of six) when the full (AE-ROCCSD/cc-pCVTZ) cubic dipole field is employed, whereas the lower-frequency band is most intense for all but one isotopologue if only the linear terms in the dipole field are utilized (Table 1). These trends might well change if the cubic dipole field were evaluated at an even higher level of theory or if matrix-isolation effects were accounted for. Given these uncertainties, the essential conclusion is that both the theoretical and experimental spectra contain bands in the $763\text{--}786\text{ cm}^{-1}$ region attributable to NCCO isotopologues and that excellent agreement is found between computed and measured isotopic shifts.

3.3 Other vibrational fundamentals

The ν_1 (CN str.) fundamental of the parent NCCO is placed at 2171 cm^{-1} by the variational vibrational computations with an intensity 16% of the corresponding ν_2 (CO str.). The experimental spectrum exhibits substantial intensity around 2170 cm^{-1} , but this region is obscured by the very strong absorption of CO and by many small, not yet identified bands of species originating from the plasma reactions (Fig. 2). While ν_4 (sym in-plane bend) should appear as a small band around 576 cm^{-1} (Table 1), considerable noise in the experimental spectrum prevents its unambiguous assignment. The bending fundamentals ν_5 and ν_6 predicted near 222 and 270 cm^{-1} , respectively, lie outside the lower limit of our spectrometer (400 cm^{-1}).

4. Conclusions

This study describes the first successful experimental infrared detection of the NCCO radical by identification of the ν_2 (CO str.) and ν_3 (CC str.) fundamentals for six of its isotopologues. A complete set of fundamental frequencies and infrared intensities has been obtained by converged variational vibrational computations based on a high-quality *ab initio* quartic force field [AE-ROCCSD(T)/cc-pCVQZ] and cubic dipole field [AE-ROCCSD/cc-pCVTZ]. The mean absolute deviation between the experimental frequencies measured here and the purely theoretical vibrational band origins is only 6.0 cm^{-1} . Moreover, the observed isotopic shifts in the ν_2 and ν_3 frequencies are in excellent accord with the theoretical predictions (mean abs. dev. = 1.1 cm^{-1}), providing very strong support for the experimental assignments. Our results for ν_1 (CN str.) (theory, 2171 cm^{-1}) and ν_2 (CO str.) (expt. 1889 cm^{-1} , theory 1898 cm^{-1}) of NCCO are drastic revisions to the frequencies deduced in earlier experiments by McNavage and Dai ($\nu_1 = 2093\text{ cm}^{-1}$, $\nu_2 = 1774\text{ cm}^{-1}$),⁴ and those compiled in the NIST-JANAF tables by Dorofeeva *et al.* ($\nu_1 = 2249\text{ cm}^{-1}$, $\nu_2 = 1703\text{ cm}^{-1}$).⁶

In the $760\text{--}805\text{ cm}^{-1}$ region, the isotopologues of NCCO exhibit two vibrational states that are strong mixtures of ν_3 (CC str.) and the $\nu_4 + \nu_5$ bending combination level. The infrared intensities for vibrational excitation to these levels are comparable due to intensity borrowing but are relatively weak. Thus, the question arises as to which state should be assigned to the ν_3 fundamental level. In the matrix-isolation FTIR spectra, only one band can be resolved in this region, which closely matches the lower energy level of the $(\nu_3, \nu_4 + \nu_5)$ Fermi resonance pair from the variational vibrational computations. For five of the NCCO isotopologues, the normal-mode decomposition of the lower-state vibrational wave function has greater proportion from ν_3 , but in the $^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$ case the $\nu_4 + \nu_5$ contribution is largest. If the ν_3 assignment is made on the basis of wave function components, then $^{14}\text{N}^{13}\text{C}^{12}\text{C}^{16}\text{O}$ displays an unusual blue-shift of the CC stretching fundamental in comparison to the $^{14}\text{N}^{12}\text{C}^{12}\text{C}^{16}\text{O}$ parent. In contrast, the expected red shift occurs if assignments are made by energetic ordering consistently across the series of isotopologues. In summary, the $(\nu_3, \nu_4 + \nu_5)$ Fermi resonance in NCCO constitutes a vivid

breakdown of the simple normal-mode approximation, and fully variational vibrational methods are required to properly describe the intricacies of this interaction.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie (Germany), by the ERA–Chemistry program, by OTKA grant K72885 (Hungary), and by the US Department of Energy (DOE), Basic Energy Sciences, Grant No. DE-FG02-97ER14718. The international collaborations received funding from the Deutsche Forschungsgemeinschaft (DFG-ERA), the Deutsche Akademische Austauschdienst (DAAD) through a PPP grant for PRS and AGC, and the Hungarian Scientific Research Fund (OTKA).

References

- 1 T. Kruse and P. Roth, *Int. J. Chem. Kinet.*, 1999, **31**, 11.
- 2 H. Y. Lee, A. M. Mebel and S. H. Lin, *Int. J. Quantum Chem.*, 2002, **90**, 566.
- 3 A. C. Simmonett, F. A. Evangelista, W. D. Allen and H. F. Schaefer, *J. Chem. Phys.*, 2007, **127**, 014306.
- 4 W. McNavage and H.-L. Dai, *J. Chem. Phys.*, 2005, **123**, 184104.
- 5 J. S. Francisco and R. F. Liu, *J. Chem. Phys.*, 1997, **107**, 3840.
- 6 O. V. Dorofeeva, V. P. Novikov and D. B. Neumann, *J. Phys. Chem. Ref. Data*, 2001, **30**, 475.
- 7 G.-T. Yu, Y.-H. Ding, X.-R. Huang, H.-T. Bai and C.-C. Sun, *J. Phys. Chem. A*, 2005, **109**, 2364.
- 8 W. J. Ding, W. H. Fang and R. Z. Liu, *Chem. Phys. Lett.*, 2002, **351**, 9.
- 9 L. Jin, Y.-H. Ding and J. Wang, *J. Theor. Comput. Chem.*, 2007, **6**, 661.
- 10 T. J. Lee, D. J. Fox, H. F. Schaefer and R. M. Pitzer, *J. Chem. Phys.*, 1984, **81**, 356.
- 11 M. E. Jacox, *J. Phys. Chem. Ref. Data*, 2003, **32**, 1.
- 12 E. Hirota, *J. Mol. Struct.*, 1986, **146**, 237.
- 13 A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez and J. F. Stanton, *J. Chem. Phys.*, 2004, **121**, 11599.
- 14 G. A. McGibbon, C. A. Kingsmill, J. K. Terlouw and P. C. Burgers, *Int. J. Mass Spectrom. Ion Processes*, 1992, **121**, R11.
- 15 A. Furlan, H. A. Scheld and J. R. Huber, *Chem. Phys. Lett.*, 1998, **282**, 1.
- 16 A. Furlan, H. A. Scheld and J. R. Huber, *J. Phys. Chem. A*, 2000, **104**, 1920.
- 17 H. A. Scheld, A. Furlan and J. R. Huber, *J. Chem. Phys.*, 1999, **111**, 923.
- 18 H. U. Suter, R. Pfister, A. Furlan and J. R. Huber, *J. Phys. Chem. A*, 2007, **111**, 764.
- 19 Y. Sumiyoshi, H. Takada and Y. Endo, *Chem. Phys. Lett.*, 2004, **387**, 116.
- 20 G. Maier, H. P. Reisenauer, J. Eckwert, C. Sierakowski and T. Stumpf, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1218.
- 21 M. E. Jacox, *Chem. Soc. Rev.*, 2002, **31**, 108.
- 22 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479.
- 23 J. D. Watts, J. Gauss and R. J. Bartlett, *J. Chem. Phys.*, 1993, **98**, 8718.
- 24 P. J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.*, 1993, **99**, 5219.
- 25 D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, 1995, **103**, 4572.
- 26 G. Simons, R. G. Parr and J. M. Finlan, *J. Chem. Phys.*, 1973, **59**, 3229.
- 27 W. D. Allen, INTDER is a general program that performs vibrational analyses and higher-order non-linear transformations among force field representations, Athens, Georgia, USA, 2005.
- 28 W. D. Allen and A. G. Császár, *J. Chem. Phys.*, 1993, **98**, 2983.
- 29 W. D. Allen, A. G. Császár, V. Szalay and I. M. Mills, *Mol. Phys.*, 1996, **89**, 1213.
- 30 K. Sarka and J. Demaison, in *Computational Molecular Spectroscopy*, ed. P. Jensen and P. R. Bunker, Wiley, Chichester, 2000, p. 255.
- 31 M. Rittby and R. J. Bartlett, *J. Phys. Chem.*, 1988, **92**, 3033.
- 32 C. Hampel, K. A. Peterson and H.-J. Werner, *Chem. Phys. Lett.*, 1992, **190**, 1.
- 33 J. D. Watts, J. Gauss and R. J. Bartlett, *Chem. Phys. Lett.*, 1992, **200**, 1.
- 34 J. F. Stanton, J. Gauss, J. D. Watts and R. J. Bartlett, *J. Chem. Phys.*, 1991, **94**, 4334.
- 35 T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny and W. D. Allen, *J. Comput. Chem.*, 2007, **28**, 1610.
- 36 W. D. Allen, INTDIF2004, an abstract program written for Mathematica (Wolfram Research Inc., Champaign, Illinois, USA) to perform general numerical differentiation to high orders of electronic structure data, Athens, Georgia, USA, 2004.
- 37 R. L. DeKock, M. J. McGuire, P. Piecuch, W. D. Allen, H. F. Schaefer, K. Kowalski, S. A. Kucharski, M. Musial, A. R. Bonner, S. A. Spronk, D. B. Lawson and S. L. Laursen, *J. Phys. Chem. A*, 2004, **108**, 2893.
- 38 E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw Hill, New York, 1955.
- 39 C. Eckart, *Phys. Rev.*, 1935, **47**, 552.
- 40 E. Mátýus, G. Czákó, B. T. Sutcliffe and A. G. Császár, *J. Chem. Phys.*, 2007, **127**, 084102.
- 41 E. Mátýus, J. Simunek and A. G. Császár, *J. Chem. Phys.*, 2009, **131**, 074106.
- 42 D. O. Harris, G. G. Engerholm and W. D. Gwinn, *J. Chem. Phys.*, 1965, **43**, 1515.
- 43 A. S. Dickinson and P. R. Certain, *J. Chem. Phys.*, 1968, **49**, 4209.
- 44 J. C. Light, I. P. Hamilton and J. V. Lill, *J. Chem. Phys.*, 1985, **82**, 1400.
- 45 J. K. G. Watson, *Mol. Phys.*, 1968, **15**, 479.
- 46 H. H. Nielsen, *Rev. Mod. Phys.*, 1951, **23**, 90.
- 47 I. M. Mills, in *Molecular Spectroscopy: Modern Research*, ed. K. N. Rao and C. W. Mathews, Academic Press, New York, 1972, p. 1.
- 48 D. A. Clabo, Jr., W. D. Allen, R. B. Remington, Y. Yamaguchi and H. F. Schaefer, *Chem. Phys.*, 1988, **123**, 187.
- 49 T. Bally, in *Reactive Intermediates*, ed. R. A. Moss, M. S. Platz and M. Jones Jr., Wiley-Interscience, Hoboken, New Jersey, 2004, p. 797.
- 50 B. Hemmerling and M. Vervloet, *Mol. Phys.*, 1993, **78**, 1423.
- 51 L. R. Brock, B. Mischler, E. A. Rohlfing, R. T. Bise and D. M. Neumark, *J. Chem. Phys.*, 1997, **107**, 665.
- 52 J. L. Duncan, A. M. Ferguson, J. Harper and K. H. Tonge, *J. Mol. Spectrosc.*, 1987, **125**, 196.
- 53 S.-H. Chen, L.-K. Chu, Y.-J. Chen, I.-C. Chen and Y.-P. Lee, *Chem. Phys. Lett.*, 2001, **333**, 365.