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Isomers of NCO₂: IR-absorption spectra of ONCO in solid Ne

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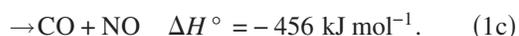
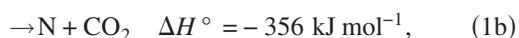
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Irradiation of a Ne matrix sample containing NO and CO near 4 K with an ArF excimer laser at 193 nm yielded new lines at 2045.1 and 968.0 cm⁻¹ that were depleted upon secondary photolysis at 308 nm. These lines are assigned to C=O stretching and mixed stretching modes of ONCO, based on results of ¹⁵N-, ¹³C-, and ¹⁸O-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP and PW91PW91/aug-cc-pVTZ) predict five stable isomers of NCO₂: ONCO, NCOO, N-*cyc*-CO₂, CNOO, and *cyc*-CNOO, listed in order of increasing energy. According to B3LYP calculations, ONCO has a *trans* configuration, with bond angles of ∠ONC ≅ 136.3° and ∠NOC ≅ 160.7°. Calculated vibrational wave numbers, IR intensities, ¹⁵N-, ¹³C-, and ¹⁸O-isotopic shifts for ONCO agree satisfactorily with experimental results. ONCO was formed from reaction of CO with NO in its excited state.

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I. INTRODUCTION

The reaction of CN with O₂ plays an important role in combustion chemistry^{1,2} and has received intensive attention in kinetic studies.³ The overall rate coefficients are about (1.3–3.0) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ near 298 K.⁴ There are three possible channels for this reaction:



Enthalpies of formation, listed in kJ mol⁻¹ in parentheses, of the following species are taken from the JANAF thermal chemical tables: CN (435.1), O (249.2), CO (-110.5), NO (90.3), N (472.7), and CO₂ (-393.5),⁵ and ΔH° = 131.7 kJ mol⁻¹ for NCO was taken from Ref. 6. Reaction (1a) is the major channel near 298 K and has been employed as a source of NCO radical in various experiments; its kinetics has been investigated extensively.⁴

Reaction (1b) is a minor channel, with a branching ratio of (2±1)% or less.³ The small branching ratio of reaction (1b) indicates that the barrier for this reaction might be large. Quantum-chemical calculations predicted this channel to proceed via formation of NCOO followed by isomerization of NCOO to N-*cyc*-CO₂ and N(CO₂) before decomposition to N(²D) and CO₂.⁷

The branching ratio for the highly exothermic channel (1c) has been determined as (22±2)%,³ (23±10)%,⁸ and

(29±2)%.⁹ Formation of CO and NO in reaction (1c) involves breaking of both C–N and O–O bonds and is likely associated with a reaction complex as an intermediate. Quantum-chemical calculations that reaction (1c) proceeds via formation of NCOO,⁷ followed by isomerization to ONCO via a barrier of ~236 kJ mol⁻¹, then dissociation to CO and NO via a barrier of ~14 kJ mol⁻¹.⁷

To our knowledge, no reaction intermediate of reaction (1) has been experimentally characterized. Among them, ONCO is predicted to have the least energy and might likely be produced in an environment at low temperature or even in the gas phase. Benson and Francisco have employed calculations at various levels up to quadratic configuration-interaction theory with perturbative correction for triples, UQCISD(T)/6-311G(2d,2p), to characterize structure, vibrational frequencies, and energy of ONCO.¹⁰ Qu *et al.* employed UB3LYP/6-31+G(d) to predict geometries of six isomers of NCO₂: ONCO, O-*cyc*-CNO, N(CO₂), NCOO, N-*cyc*-CO₂, and CNOO, listed in increasing order of energy calculated with UCCSD(T)/6-311+G(d) with inclusion of the zero-point vibrational-energy corrections calculated with Becke's three-parameter hybrid exchange functional and a correlation functional of Lee, Yang, and Parr (B3LYP) method.⁷

Utilizing selective photodissociation with a laser to avoid secondary photolysis of species of interest,^{11–14} we produced numerous novel species by either photolysis of a precursor *in situ*^{15–20} or by further reactions of photofragments with a nearest neighbor upon photolysis;^{21–24} these species are difficult to produce in the gaseous phase using conventional techniques. Here we report a theoretical investigation of possible isomers of NCO₂ and the experimental preparation and infrared identification of ONCO by irradiation

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tion of Ne matrix samples containing NO and CO with laser emission at 193 nm to induce the reaction of CO with electronically excited NO.

II. EXPERIMENTS

The experimental setup is similar to that described previously.^{15,20} A nickel-plated copper plate cooled to ~ 4 K serves as a cold substrate for a matrix sample and as a mirror to reflect incident infrared (IR) beam to the detector. A new closed-cycle cryogenic system (Janis RDK-415) was employed to cool the target to 3.5 K. Typically, a gaseous mixture of 0.006 mol of CO/NO/Ne (1/1/1000) was deposited over a period of 2 h. An ArF excimer laser (193 nm, operated at 10 Hz with energy of ~ 6 mJ pulse⁻¹) was employed to excite NO. A XeCl excimer laser (308 nm, operated at 10 Hz with energies of ~ 3 mJ pulse⁻¹) was used for secondary photolysis. IR-absorption spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (Bomem, DA8) equipped with a KBr beam splitter and a Hg/Cd/Te detector (cooled to 77 K) to cover the spectral range of 500–4000 cm⁻¹. Typically 600 scans with resolution of 0.5 cm⁻¹ were recorded at each stage of the experiment.

¹³CO (isotopic purity 99%) and N¹⁸O (isotopic purity $\sim 70\%$, both Cambridge Isotope Laboratories) were used without further purification. ¹⁵NO was synthesized by slow addition of 10% (by mass) sulfuric acid solution into Na¹⁵NO₂ (isotopic purity 99%); produced gases were passed through a trap of KOH to remove HNO₃ and trapped at 77 K. Ne (99.999%, Scott Specialty Gases) was used without further purification.

III. COMPUTATIONAL METHOD

The equilibrium structures, vibrational frequencies, IR intensities, and energies were calculated with the GAUSSIAN 03 program.²⁵ We used two types of density-functional theory (DFT) for calculations. The B3LYP method uses Becke's three-parameter hybrid exchange functional,²⁶ and a correlation functional of Lee, Yang, and Parr,^{27,28} with both local and nonlocal terms. The PW91PW91 method uses exchange and correlation functionals of Perdew and Wang.²⁹ Dunning's correlation-consistent polarized valence triplet-zeta basis set, augmented with *s*, *p*, *d*, and *f* functions (aug-cc-pVTZ), was used in all methods. Analytic first derivatives were utilized in geometry optimization, and vibrational wave numbers were calculated analytically at each stationary point.

IV. RESULTS AND DISCUSSION

A. Experimental observations and assignments

1. Experiments with irradiated CO and NO in natural abundance

The IR spectrum of a sample of CO/NO/Ne (1/1/1000) at 4 K exhibits lines due to CO (2140.9 cm⁻¹), CO₂ (2347.7 cm⁻¹), NO (1874.8 cm⁻¹), and *c*-(NO)₂ (1778.7 cm⁻¹).³⁰ Weak lines at 2094.4 and 2283.0 cm⁻¹ are due to ¹³CO and ¹³CO₂, respectively. A partial spectrum of the matrix sample after deposition is shown

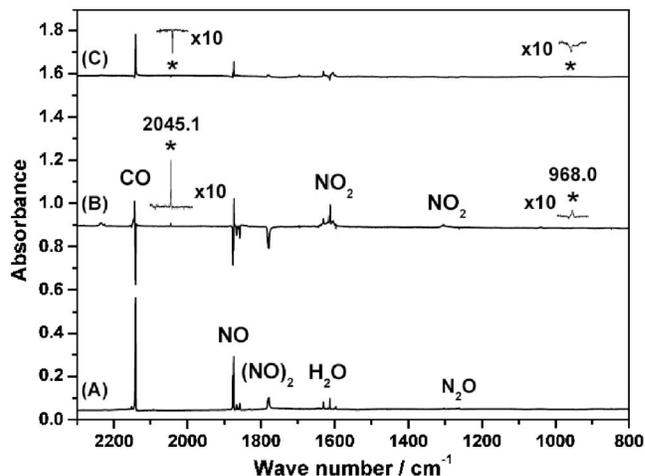


FIG. 1. Partial IR absorption spectrum of a CO/NO/Ne (1/1/1000) matrix sample before irradiation (A), difference spectrum after irradiation at 193 nm for 180 min (B), and difference spectrum after further irradiation of the matrix at 308 nm for 20 min (C). New lines are marked as *.

in trace A of Fig. 1. Trace B of Fig. 1 is a difference spectrum recorded after irradiation of the matrix sample at 193 nm for 3 h. The difference spectrum was derived on subtracting the spectrum recorded in the preceding stage of irradiation/annealing from a new spectrum; a positive feature indicates production, whereas a negative feature indicates destruction.

After irradiation, intensities of lines due to CO and NO decreased by $\sim 50\%$ and lines due to CO₂ (2347.7 cm⁻¹), NO₂ (1304.1 and 1618.2 cm⁻¹), N₂O (1285.0 cm⁻¹) appeared. New lines at 2045.1 and 968.0 cm⁻¹ [marked * in Fig. 1(b)] were also observed; the latter exhibits an intensity of $\sim 5\%$ of the former. Further irradiation of the matrix sample with laser emission at 308 nm for 20 min diminished these new lines substantially, as illustrated in the difference spectrum shown in trace C of Fig. 1. CO and NO appeared as major products upon secondary photolysis; integrated intensities indicate that about 30% of the new species was

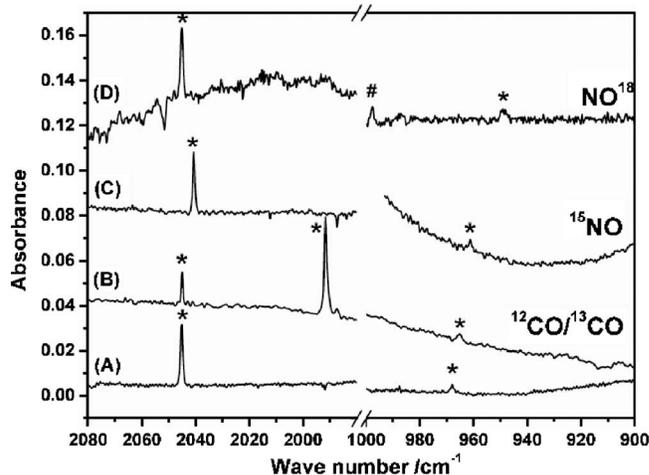


FIG. 2. Partial difference IR absorption spectra of lines from CO/NO/Ne matrix samples with isotopic variants after irradiation at 193 nm for 180 min. (A) CO/NO/Ne (1/1/1000), (B) ¹²C/¹³C/NO/Ne (1/4/1/1000), (C) CO/¹⁵N/NO/Ne (1/1/1000), and (D) CO/N¹⁶O/Ne (4/0.2/0.8/1000). New lines are marked as *.

TABLE I. Wave numbers (in cm^{-1}) of lines observed for various isotopically labeled CO/NO/Ne matrix samples after irradiation at 193 nm.

Species	C=O stretch (ν_1)	Mixed stretch (ν_3)
$^{16}\text{O}^{14}\text{N}^{12}\text{C}^{16}\text{O}$	2045.1	968.0
$^{16}\text{O}^{14}\text{N}^{13}\text{C}^{16}\text{O}$	1991.2	964.9
$^{16}\text{O}^{15}\text{N}^{12}\text{C}^{16}\text{O}$	2040.9	961.0
$^{18}\text{O}^{14}\text{N}^{12}\text{C}^{16}\text{O}$	2045.0	948.6

decomposed and about $(20 \pm 5)\%$ of CO and NO were reproduced. After annealing of the irradiated matrix to 7 K, these new lines at 2045.1 and 968.0 cm^{-1} did not regain their intensities.

2. ^{13}C -isotopic experiments

An isotopic mixture with $^{12}\text{CO}/^{13}\text{CO}/\text{NO}/\text{Ne} = 1/4/1/1000$ was used in one experiment. A difference spectrum of the matrix sample in regions 900–1000 and 1980–2080 cm^{-1} recorded after laser irradiation at 193 nm for 3 h is shown in trace B of Fig. 2; trace A of Fig. 2 depicts the corresponding difference spectrum of a CO/NO/Ne = 1/1/1000 matrix sample in natural abundance. Wave numbers of new lines for all isotopic species are listed in Table I.

The line at 2045.1 cm^{-1} splits into two lines with the wave number of the additional line at 1991.2 cm^{-1} . The mixed ^{12}C - and ^{13}C -isotopic pattern indicates that only one C atom is involved in this mode. The ^{13}C -isotopic ratio $1991.2/2045.1 = 0.9736$, defined as a ratio of vibrational wave number of the isotopically labeled species to that of the most naturally abundant species, is slightly smaller than the theoretical value of 0.9778 for stretching of diatomic CO, indicating that the C atom might be bound to another atom.

The weak line at 968.0 cm^{-1} shifts to 964.9 cm^{-1} ; the original line at 968.0 cm^{-1} is too weak to be observed. The ^{13}C -isotopic ratio of $964.9/968.0 = 0.9968$ is much greater than the corresponding value of 0.9736 for the line at 2045.1 cm^{-1} . The ^{13}C -isotopic pattern indicates that one C atom is perhaps indirectly involved in this mode.

3. ^{15}N -isotopic experiments

An isotopic mixture with CO/ $^{15}\text{NO}/\text{Ne} = 1/1/1000$ was used in one experiment. A difference spectrum of the matrix sample recorded after irradiation at 193 nm for 3 h is shown in trace C of Fig. 2. Wave numbers of new lines are listed in Table I. The line at 2045.1 cm^{-1} shifts slightly to 2040.9 cm^{-1} . The ^{15}N -isotopic ratio $2040.9/2045.1 = 0.9979$ is close to but smaller than unity, indicating that the N atom is only slightly involved in this mode; it might be bound to the C atom.

The weak line at 968.0 cm^{-1} shifts to 961.0 cm^{-1} . The ^{15}N -isotopic ratio of $961.0/968.0 = 0.9928$ is smaller than the corresponding value of 0.9968 for the ^{13}C -isotopic ratio, indicating that involvement of N atom is greater than that of C atom in this mode.

4. ^{18}O -isotopic experiments

A difference spectrum of a matrix sample at CO/ $^{16}\text{O}/^{18}\text{O}/\text{Ne} = 4/0.2/0.8/1000$ after laser irradiation at 193 nm is shown in trace D of Fig. 2; line positions of ^{18}O -substituted species are also listed in Table I. The line at 2045.1 cm^{-1} remains almost unshifted upon ^{18}O -isotopic substitution. The ^{18}O -isotopic ratio $2045.0/2045.1 = 0.9999$ is near unity, indicating that this O atom from NO likely is not bound to the C atom. The line at 968.0 cm^{-1} shifts to 948.6 cm^{-1} ; the line for ^{16}O -species is too weak to be identified. The ^{18}O -isotopic ratio of $948.6/968.0 = 0.9799$ is near the theoretical value of 0.9737 for NO. The ^{18}O -isotopic pattern indicates that likely one O atom from NO is involved in this mode.

5. Assignments

The photons at 193 nm can excite NO to its electronic excited state but the energy is too small to break either the C–O or the N–O bond; hence one would expect CO and NO to remain intact during the reaction. Reaction between CO and NO in a matrix is expected to produce either ONCO or NCOO. Because observed isotopic patterns indicate that the species contains a C=O moiety with perhaps a N atom connected to the C atom and the O atom from NO is nearly uninvolved with the observed C–O stretching mode, the new

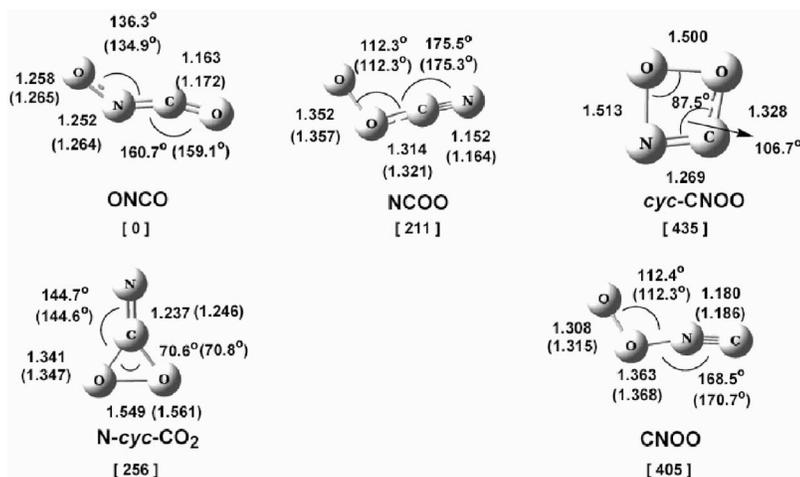


FIG. 3. Geometries and relative energies (in kJ mol^{-1}) of isomers of NCO_2 calculated with the B3LYP/aug-cc-pVTZ method; these energies are corrected with zero-point energies and listed in brackets. The unit of bond length is Å. Results from UB3LYP/6-31+G(d) in Ref. 7 are listed in parentheses.

TABLE II. Vibrational wave numbers (in cm^{-1}) and infrared intensities (in km mol^{-1} , listed in parentheses) of ONCO and CNOO predicted with various theoretical methods.

Species	Vibrational mode	QCISD(T) /6-31G*	B3LYP /aug-cc-pVTZ	PW91PW91 /aug-cc-pVTZ	Experiment /Ne matrix
ONCO	ν_1 , CO stretch	2137 (514)	2156.3 (494)	2025.5 (247)	2045.1
	ν_2 , NO stretch	1328 (21)	1420.0 (38)	1444.6 (138)	
	ν_3 , mixed stretch	963 (28)	966.0 (21)	910.7 (7)	968.0
	ν_4 , in-phase bend	611 (24)	548.8 (23)	490.0 (6)	
	ν_5 , oop def. ^a	336 (20)	352.4 (19)	293.6 (25)	
	ν_6 , out-of-phase bend	213 (16)	255.1 (23)	279.1 (9)	
CNOO	ν_1 , CN stretch		2109.6 (246)		
	ν_2 , OO stretch		1081.6 (2)		
	ν_3 , NO stretch		763.7 (13)		
	ν_4 , NOO bend		544.2 (5)		
	ν_5 , CNO oop def. ^a		182.4 (0)		
	ν_6 , CNO bend		124.3 (1)		
		^b	This work	This work	This work

^aOut-of-plane deformation.^bReference 10.

species is likely ONCO rather than NOCO and the line at 2045.1 cm^{-1} is assigned to its $\text{C}=\text{O}$ stretching mode.

The isotopic ratios for the line at 968.0 cm^{-1} provide insufficient information for definitive assignment. The substantial ^{18}O -isotopic ratio from $\text{CO}/\text{N}^{18}\text{O}$ experiments indicates that this line is associated with $\text{N}-\text{O}$ stretching mode, but the ^{15}N -isotopic ratio is smaller than expected. This line might be associated with a mixed mode; the large ^{18}O shift and the smaller ^{15}N shift are consistent with a structure of ONCO having a terminal O atom in the NO moiety. Quantum-chemical calculations are expected to provide further information for the assignments.

B. Comparison with calculations

We performed calculations with the B3LYP method using the aug-cc-pVTZ basis set to locate five stable isomers of NCO_2 : ONCO, NCOO, *N-cyc-CO*₂, CNOO, and *cyc-CNOO*, listed in order of increasing energy. NOCO was predicted to be unstable. Geometries and energies predicted with B3LYP/aug-cc-pVTZ for these species are shown in Fig. 3, with geometries predicted previously by Qu *et al.*⁷ using UB3LYP/6-31+G(*d*) listed parenthetically for comparison. In previous work with a smaller basis set, isomers $\text{N}(\text{CO}_2)$ and *O-cyc-CON* were predicted to be stable,⁷ but the stable configuration *cyc-CNOO* was not reported. The most stable isomer ONCO, predicted with B3LYP/aug-cc-pVTZ, has bond lengths of $\text{O}-\text{N}$, $\text{N}-\text{O}$, and $\text{C}-\text{O}$ of 1.258, 1.252, and 1.163 Å, respectively, similar to corresponding values of 1.265, 1.264, and 1.172 Å calculated previously with UB3LYP/6-31+G(*d*),⁷ and 1.266, 1.283, and 1.169 Å with UQCISD(T)/6-311G(2*d*,2*p*).¹⁰ Bond angles of ONCO of 136.3° for $\angle\text{ONC}$ and 160.7° for $\angle\text{NCO}$ are similar to corresponding values of 134.9° and 159.1° from UB3LYP/6-31+G(*d*) (Ref. 7) and 132.8° and 156.2° from UQCISD(T)/6-311G(2*d*,2*p*).¹⁰

Isomers NCOO and *N-cyc-CO*₂ are predicted to lie ~ 211 and 256 kJ mol^{-1} above ONCO; previous

calculations⁷ using CCSD(T)/UB3LYP/6-31+G(*d*) predicted similar values, with energies 189 and 229 kJ mol^{-1} , respectively. The other two stable isomers, CNOO and *cyc-CNOO*, have much greater energies: 405 and 435 kJ mol^{-1} above ONCO.

Table II compares vibrational wave numbers, approximate mode description, and infrared intensities of NCO_2 predicted with the B3LYP and PW91PW91 methods in this work and QCISD/6-31G(*d*) reported previously.¹⁰ Table III lists vibrational wave numbers and infrared intensities of NCOO, *N-cyc-CO*₂, and *cyc-CNOO* predicted with the B3LYP. Observed vibrational wave numbers of new lines at 2045.1 and 968.0 cm^{-1} are near the values 2156 and 966 cm^{-1} from B3LYP and 2026 and 911 cm^{-1} from PW91PW91 predicted for ν_1 ($\text{C}=\text{O}$ stretching) and ν_3 (mixed stretching) modes of ONCO, respectively, but distinct from values predicted for other isomers of NCO_2 . The possibility that observed new lines are associated with CNOO cannot be completely eliminated because its ν_1 ($\text{C}-\text{N}$ stretching) and ν_2 ($\text{O}-\text{O}$ stretching) modes were predicted with B3LYP to be 2110 and 1082 cm^{-1} , corresponding to deviations of 3% and 12%, respectively. The observed ratio of integrated intensities for lines at 2045.1 and 968.0 cm^{-1} , $\sim 14:1$, agrees satisfactorily with the ratio 23:1 predicted for ν_1 and ν_3 of ONCO with the B3LYP method. The ν_2 mode of ONCO was predicted to lie at $\sim 1420 \text{ cm}^{-1}$ with an IR inten-

TABLE III. Vibrational wave numbers and infrared intensities (listed in parentheses) of NCOO, *N-cyc-CO*₂, and *cyc-CNOO* predicted with B3LYP/aug-cc-pVTZ.

Species	Vibrational wave numbers (cm^{-1}) and IR intensity (km mol^{-1})
NCOO	2315 (5), 1060 (23), 983 (2), 636 (3), 445 (11), 254 (8)
<i>N-cyc-CO</i> ₂	1831 (109), 1102 (14), 886 (48), 703 (7), 559 (14), 459 (24)
<i>cyc-CNOO</i>	1550 (16), 1218 (53), 989 (16), 741 (2), 576 (1), 502 (0)

TABLE IV. Comparison of IR wave numbers (in cm^{-1} , listed only for the isotopomers in major natural abundance) and ^{13}C -, ^{15}N -, and ^{18}O -isotopic ratios (defined as the ratio of vibrational wave numbers of a substituted isotopomer to that of the corresponding ^{13}C -, ^{15}N -, and ^{18}O -species) of ONCO and CNOO.

Species		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$^{16}\text{O}^{14}\text{N}^{12}\text{C}^{16}\text{O}$	Calc.	2156.3	1420.0	966.0	548.8	352.4	255.1
	Expt.	2045.1		968.0			
$^{16}\text{O}^{14}\text{N}^{13}\text{C}^{16}\text{O}$	Calc.	0.9732	0.9998	0.9953	0.9784	0.9716	0.9926
	Expt.	0.9736		0.9968			
$^{16}\text{O}^{15}\text{N}^{12}\text{C}^{16}\text{O}$	Calc.	0.9980	0.9784	0.9931	0.9925	0.9998	0.9887
	Expt.	0.9979		0.9928			
$^{18}\text{O}^{14}\text{N}^{12}\text{C}^{16}\text{O}$	Calc.	0.9999	0.9871	0.9783	0.9933	0.9976	0.9840
	Expt.	0.9999		0.9799			
$^{16}\text{O}^{14}\text{N}^{12}\text{C}^{18}\text{O}$	Calc.	0.9863	0.9934	0.9775	0.9936	0.9874	0.9883
$^{12}\text{C}^{14}\text{N}^{16}\text{O}^{16}\text{O}$	Calc.	2109.6	1081.6	763.7	544.2	182.4	124.3
$^{13}\text{C}^{14}\text{N}^{16}\text{O}^{16}\text{O}$	Calc.	0.9815	0.9986	0.9973	0.9909	0.9887	0.9757
$^{12}\text{C}^{15}\text{N}^{16}\text{O}^{16}\text{O}$	Calc.	0.9829	0.9992	0.9938	0.9886	0.9756	0.9761
$^{12}\text{C}^{14}\text{N}^{18}\text{O}^{16}\text{O}$	Calc.	0.9998	0.9730	0.9637	0.9885	0.9949	0.9869
$^{12}\text{C}^{14}\text{N}^{16}\text{O}^{18}\text{O}$	Calc.	0.9999	0.9730	0.9911	0.9847	0.9980	0.9800

sity of $\sim 8\%$ of ν_1 , but we could not positively identify this line partly because of the small intensity and partly because it might be overlapped with the absorption of NO_2 near the 1300 cm^{-1} region.

Table IV lists ^{13}C -, ^{15}N -, and ^{18}O -isotopic ratios of ONCO and CNOO predicted with B3LYP/aug-cc-pVTZ; as those predicted with PW91PW91 are similar, they are omitted. Predicted isotopic ratios for ONCO are nearly the same as available experimental data. Isotopic ratios predicted for CNOO do not agree with our experimental results. It should be noted that even though vibrational wave numbers for ν_1 and ν_3 of ONCO predicted with B3LYP or PW91PW91 vary by as much as 5%, corresponding isotopic ratios vary by less than 0.15%. According to predicted vector displacements, ν_3 is associated with a mixed stretching mode that may be described approximately as a breathing mode with stretching of O–N, N–C, and C–O bonds contributing about 41%, 13%, and 46%, respectively, of the motion; hence the major isotopic shifts for ν_3 are resulting from terminal O atoms, as shown in Table IV.

Hence, based on observed ^{13}C -, ^{15}N -, and ^{18}O -isotopic shifts and comparison with vibrational wave numbers and isotopic ratios predicted with quantum-chemical calculations, we conclude that *new absorption lines at 2045.1 and 968.0 cm^{-1} are associated with C=O stretching (ν_1) and mixed stretching (ν_3) modes of ONCO isolated in solid Ne.*

C. Mechanism of formation of ONCO

The first electronically excited singlet state of CO lies at $64\,748\text{ cm}^{-1}$,³¹ inaccessible to irradiation at 193 nm ($51\,813\text{ cm}^{-1}$). In contrast, the absorption band for the $A\ ^2\Sigma^+ - X\ ^2\Pi$ transition of NO in a Ne matrix, lying near $51\,934\text{ cm}^{-1}$ with full width at half maximum (FWHM) of 1451 cm^{-1} ,³² overlaps with the irradiation at 193 nm. Production of ONCO upon irradiation is hence due to reaction of CO with electronically excited NO as a nearest neighbor. That annealing of the matrix at 7 K did not increase the intensity of ONCO indicates that production of ONCO is not

from direct reaction of NO and CO. Theoretical calculations with UCCSD(T)/6-311+G(d) predict a barrier of $\sim 159\text{ kJ mol}^{-1}$ for formation of ONCO from $\text{NO} + \text{CO}$, making this reaction inaccessible at low temperature.⁷

When the CO/NO/Ne sample irradiated at 193 nm was irradiated further at 308 nm, lines due to ONCO disappeared, whereas lines due to CO and NO increased. This observation indicates that ONCO likely photodissociates at 308 nm to break the C–N bond. We performed time-dependent density-functional theory (TDDFT) using the B3LYP/aug-cc-pVTZ method to investigate electronically excited states of ONCO and found that its third excited state ($2\ ^2A''$) lies $\sim 33\,967\text{ cm}^{-1}$ above the ground $X\ ^2A''$ state and that the transition involves excitation of an electron associated with the C–N π -bonding orbital ($3A''$) to the C–N π -anti-bonding orbital; dissociation of the C–N bond is hence expected.

V. CONCLUSION

We irradiated matrix samples of CO/NO/Ne near 4 K with an ArF excimer laser at 193 nm and observed new IR-absorption lines at 2045.1 and 968.0 cm^{-1} . These new features are attributed to C=O stretching (ν_1) and mixed stretching (ν_3) modes of ONCO, based on observed ^{13}C -, ^{15}N -, and ^{18}O -isotopic shifts and theoretical predictions of line positions, infrared intensities, and isotopic ratios for possible isomers of NCO_2 . The product ONCO is likely formed via reaction of CO with neighboring electronically excited NO in the matrix; secondary photolysis at 308 nm depleted ONCO and produced mainly CO and NO.

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