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Vibrations of nitrous oxide: Matrix isolation Fourier transform infrared spectroscopy of twelve N₂O isotopomers

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(Received 30 March 2001; accepted 10 May 2001)

Isotopically labeled nitrous oxide has been produced in solid nitrogen matrices using mixtures of nitrogen and water containing ¹⁴N, ¹⁵N, ¹⁶O, ¹⁷O, and ¹⁸O. All twelve possible N₂O isotopomers have been obtained, and their fundamental, overtone and combination frequencies were assigned by the joint use of infrared spectroscopy and quantum chemical calculations (B3LYP/AUG-cc-pVTZ). Specific influence of the nitrogen matrix upon frequency and anharmonicity of the vibrations has been discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1383031]

I. INTRODUCTION

Nitrous oxide, N₂O, discovered by Priestley in 1793, and dubbed “laughing gas” by Davy shortly afterwards, is widely known for its anesthetic properties. More important, it is one of the greenhouse gases, with a capacity to trap heat in the atmosphere more than two orders of magnitude larger than that of CO₂.^{1,2} Its IR absorption range fills the gap between the regions of absorption of water and CO₂. N₂O also participates in the stratospheric ozone cycle.^{3,4} The concentration of N₂O in the atmosphere is increasing at a rate of 0.25%/year, mostly due to agricultural soil management and fuel combustion. The atmospheric residence time of N₂O is about 150 years; it is destroyed through photolysis (90%), yielding N₂ and O, and by photooxidation that leads either to two molecules of NO (6%) or to N₂ and O₂ (4%).

In spite of numerous studies,^{5–17} the global budget of nitrous oxide and the mechanisms of its formation and decay are still not well understood. A powerful tool for identification of its sources and sinks is the isotopic characterization of N₂O collected from different locations (oceans, soils, atmosphere). When applied to atmospheric chemistry, this procedure led to divergent interpretations. Stratospheric N₂O is enriched in ¹⁵N and ¹⁸O.^{5–8} On the basis of measurements of ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, and ¹⁷O/¹⁶O ratios in atmospheric samples, some authors suggested the existence of a previously undefined atmospheric process.^{6–8} An alternative explanation was proposed,⁹ that assumed different yields of

photolysis of various isotopomers. In particular, the ¹⁵N¹⁴N¹⁶O and ¹⁴N¹⁵N¹⁶O species were postulated to have very different isotopic fractionations in the atmosphere as a result of different ground state zero point vibrational energies (ZPEs). The experimental evidence supporting this hypothesis has been provided recently.^{10,17–19}

It becomes obvious in the above context that a desired property of an analytical method used to study isotopic composition should be the ability to determine the intramolecular position of the nitrogen isotope in N₂O. This is not the case with conventional mass spectrometry, although a modified spectrometer, able to perform this task, has recently been described.²⁰ Laboratory procedures based on workup of field samples require attention, in order to avoid artifacts, such as surface reactions or contamination with CO₂. *In situ* measurements are evidently preferable, with infrared spectroscopy as an attractive choice. Fourier transform infrared (FTIR) (Refs. 21–25) and tunable diode laser^{26–29} instruments have been described that are able to operate onboard a shuttle or aircraft. These measurements can use an extensive data basis of gas phase rovibrational N₂O spectra, accumulated over several decades.^{30–83} High-resolution IR measurements for N₂O have been performed with great accuracy, and the obtained data serve as standards in wavenumber calibration tables.^{62,73,80–83} Moreover, IR studies provide the ZPEs necessary for calculating fractionation factors for various isotopomers. Substantial effort has been devoted to the determination of the force field for N₂O.^{84–94}

Much less is known about vibrational spectroscopy of

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nitrous oxide in condensed phases. Cryogenic studies involving N_2O have been reported in several papers.^{95–113} The spectra of the parent $^{14}\text{N}_2^{16}\text{O}$ species were obtained in solid N_2O ,⁹⁵ argon,^{97–101} nitrogen,^{96,102–104} and xenon^{101,105} matrices. Matrix-isolated N_2O has also been used as a source of molecular ions^{106–110} and as a reagent with laser-ablated metal atoms.^{111,112} The experimental data for isotopically substituted species are very scarce. IR frequencies have only been reported for the three fundamentals and several other bands of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}_2^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, and $^{15}\text{N}^{14}\text{N}^{18}\text{O}$ in nitrogen and argon matrices.^{96,98,99} No systematic investigation of all isotopomers has been performed so far. In this work, we present a vibrational study of matrix-isolated isotopomers of N_2O , obtained in a microwave discharge of water-containing mixtures with nitrogen. Using ^{15}N , ^{17}O , and ^{18}O isotopically labeled species resulted in the production of all possible twelve isotopomers. Combined use of matrix-isolation FTIR spectroscopy and quantum chemical computations enabled a complete characterization of vibrational patterns. It is hoped that the obtained results can contribute to practical applications, such as environmental control, and to further development of the theoretical investigation of this important molecule.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Various isotopically labeled oxides of nitrogen (nitrous oxide, N_2O ; nitric oxide, NO ; nitrogen dioxide, NO_2 ; and dinitrogen tetroxide, N_2O_4), as well as several isotopic compositions of ozone were prepared in the gas-phase by reacting atomic or molecular nitrogen with oxygen. The gaseous dinitrogen [$^{14}\text{N}_2$, $^{15}\text{N}_2$ (98 + % ^{15}N , Cambridge Isotope Laboratories) or 1:1 mixture] was passed in the glass or quartz tube through a 2450 MHz microwave cavity. In some experiments we have used 30 kV electrical discharge between two electrodes attached to the deposition tube. The ^{18}O was introduced from 95%–98% ^{18}O -labeled water, while ^{17}O was added from 50% labeled water (Cambridge Isotope Laboratories). The reaction mixture was condensed onto a cold (6.5 K) salt window (CsI or BaF_2) attached to the tip of the closed-cycle helium refrigerator (DE-202A-N, APD-Cryogenics). The infrared spectra were measured on a Nicolet-560 FTIR spectrometer with 0.125 cm^{-1} resolution.

In some experiments, oxygen, neon, krypton or xenon were added to the deposition mixture, to check for the possible formation of complexes with oxygen and to determine spectral shifts in different matrices.

The molecular equilibrium geometry and harmonic force field^{114,115} for N_2O were computed with the GAUSSIAN 94 and GAUSSIAN 98 software packages^{116,117} by using B3LYP density functional theory^{118,119} and the AUG-cc-pVTZ basis set.¹²⁰ Numerous structure and force field calculations reported for nitrous oxide^{89–94,121–127} have shown that obtaining reliable results for both geometry and vibrational frequencies requires an extensive treatment of electron correlation and large basis sets. Our calculated values for N–N and N–O distances, 1.121 Å and 1.184 Å, respectively, are in excellent agreement with the experimental values of 1.127 Å and 1.185 Å.⁸⁷ Values of similar accuracy, 1.131 Å and 1.186 Å, were recently calculated using CASPT2(10,9)/

cc-pVTZ level of theory.¹²¹ Interestingly, it was shown in the same work that the computational results are significantly influenced by using only slightly smaller active space or basis set: The agreement with experiment was found to be much worse for CASPT2(10,9)/cc-pVDZ and CASPT2(10,8)/cc-pVDZ levels.

The dipole moment predicted with B3LYP/AUG-cc-pVTZ is 0.076 D, with the negative end pointing towards the oxygen atom; the experimental gas phase value is 0.166 D.¹²⁸ This theoretical prediction should be considered very satisfactory, given that the calculated value of the dipole moment of N_2O is very sensitive to the value of interatomic distances and the extent of electron correlation. It has been shown¹²⁶ that SCF and SDCI methods yield a correct sign, $^+\text{NNO}^-$, but the computed values are too large. On the other hand, MP2 produces a value close to the experimental one, but yields an incorrect sign.

III. RESULTS AND DISCUSSION

In the gas phase, the frequencies corresponding to the fundamental stretching (ν_3 and ν_1 , Σ^+ symmetry species) and bending (ν_2 , Π symmetry species) vibrations of N_2O are 2223.8, 1284.9, and 588.8 cm^{-1} , respectively.^{41,42} Portions of the IR spectra recorded in corresponding spectral regions in nitrogen matrices at 10 K are presented in Figs. 1–3. Using equimolar mixtures of isotopomers of nitrogen led to practically the same intensities of the product bands. Hence, starting from a 1:1 mixture of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ produced equal amounts of $^{14}\text{N}_2^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, and $^{15}\text{N}_2^{16}\text{O}$. This implicates that the isotope scrambling is complete, and thus, that the products are obtained from nitrogen atoms.

Assignments of vibrational bands to particular isotopomers were achieved by comparing patterns observed for samples of various isotopic compositions, by referring to previously reported matrix and gas phase data, and by comparing experimentally observed frequencies with the calculated ones. The results are compiled in Tables I–V. Our frequencies agree to within 0.2 cm^{-1} with those recently reported for nitrogen matrix.¹⁰³ With regard to the data obtained on a dispersive instrument with lower spectral resolution,⁹⁶ the largest differences, about 1–2 cm^{-1} are observed in the lower energy region (ν_2 fundamental) and for combination bands lying above 3000 cm^{-1} .

In the vicinity of the ν_1 and ν_3 bands, weak features are observed. The relative intensity of these features depends on the mode of sample preparation. In accordance with the results of recent work,^{103,104} we assign these bands to complexes of N_2O with molecular oxygen. We have verified these assignments by performing experiments in which oxygen was being gradually added to the deposition mixture. This led to significant growth of satellite bands.

In an early study in a nitrogen matrix,⁹⁶ and in the investigation of solid N_2O ,⁹⁵ the bands observed at 1885.9 cm^{-1} and at 1891 cm^{-1} , respectively, were assigned to $\nu_1 + \nu_2$ combination. In a recent paper, this assignment was made for a band at 1866.3 cm^{-1} .¹⁰³ We have observed both bands in this region, the former of much weaker intensity. We assign the $\nu_1 + \nu_2$ combination to the band detected at 1885.3 cm^{-1} (Table V), in accordance with the finding that,

TABLE I. Experimental and calculated frequencies for the ν_3 vibration and the isotopic shifts with respect to parent $^{14}\text{N}^{14}\text{N}^{16}\text{O}$.

	Frequency (cm^{-1})		Isotopic shift (cm^{-1})	
	Experiment ^a	Calculated ^b	Experiment ^a	Calculated ^b
$^{14}\text{N}^{14}\text{N}^{16}\text{O}$	2235.6 (2223.8)	2339.5
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	2212.9 (2201.6)	2314.7	22.7 (22.2)	24.8
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	2188.8 (2177.7)	2289.8	46.8 (46.1)	49.7
$^{15}\text{N}^{15}\text{N}^{16}\text{O}$	2165.6 (2154.7)	2264.2	70.0 (69.1)	75.3
$^{14}\text{N}^{14}\text{N}^{17}\text{O}$	2232.0 (2220.1)	2336.6	3.6 (3.7)	2.9
$^{15}\text{N}^{14}\text{N}^{17}\text{O}$	2209.4 (2197.6)	2311.2	26.2 (26.2)	28.3
$^{14}\text{N}^{15}\text{N}^{17}\text{O}$	2185.7 (2174.2)	2286.6	49.9 (49.6)	52.9
$^{15}\text{N}^{15}\text{N}^{17}\text{O}$	2162.4 (2150.9)	2260.7	73.2 (72.9)	78.8
$^{14}\text{N}^{14}\text{N}^{18}\text{O}$	2228.7 (2216.7)	2336.6	6.9 (7.1)	2.9
$^{15}\text{N}^{14}\text{N}^{18}\text{O}$	2205.9 (2194.0)	2308.4	29.7 (29.8)	31.1
$^{14}\text{N}^{15}\text{N}^{18}\text{O}$	2182.7 (2171.0)	2284.1	52.9 (52.8)	55.4
$^{15}\text{N}^{15}\text{N}^{18}\text{O}$	2159.1 (2147.6)	2257.9	76.5 (76.2)	81.6

^aGas phase values in parentheses (from Refs. 44, 51–54, 86).^bB3LYP/AUG-cc-pVTZ; see text.

in nitrogen matrices, the values of the six combination bands involving ν_2 that we observed are always higher than the corresponding gas phase values (see Table V).

The intensity pattern for the three fundamental transitions is practically the same for all isotopomers. The strongest band, corresponding to ν_3 , is about five times more intense than the band corresponding to ν_1 and about 35 times stronger than the ν_2 transition. The intensity ratios are similar to those observed in the gas phase,^{61,73} and are consistent with the intensities predicted by B3LYP/AUG-cc-pVTZ: $I = 396, 70$, and 10 km/mol for ν_3 , ν_1 , and ν_2 , respectively.

A. ν_3 vibration (Table I and Fig. 1)

The frequency for the parent $^{14}\text{N}_2^{16}\text{O}$ species is 2235.6 cm^{-1} ; exactly the same value was previously reported for the nitrogen matrix.¹⁰³ Interestingly, a large blue shift with respect to the gas phase is observed, nearly constant for all isotopomers and ranging from 10.9 cm^{-1} for $^{15}\text{N}_2^{16}\text{O}$ to 12.0 cm^{-1} for $^{14}\text{N}_2^{18}\text{O}$. A blue shift was also encountered in solid $^{14}\text{N}_2\text{O}$, where the frequency is 2238 cm^{-1} .⁹⁵ This effect seems to be specific for the nitrogen-containing matrices: In argon¹⁰⁰ and xenon matrices¹⁰⁵ and xenon free-standing crystals¹⁰¹ red shifts of $5.2, 9.3$, and 9.0 cm^{-1} , respectively, have been detected. Adding krypton to deposition mixtures, we have observed several sites, of which the strongest was redshifted with respect to the gas phase by 4.9 cm^{-1} .

The shifts observed after an isotopic substitution at a particular position reflect the character of the vibration, which is essentially an $\text{N}\equiv\text{N}$ stretch, with the amplitude of vibration of the central nitrogen atom much larger than that

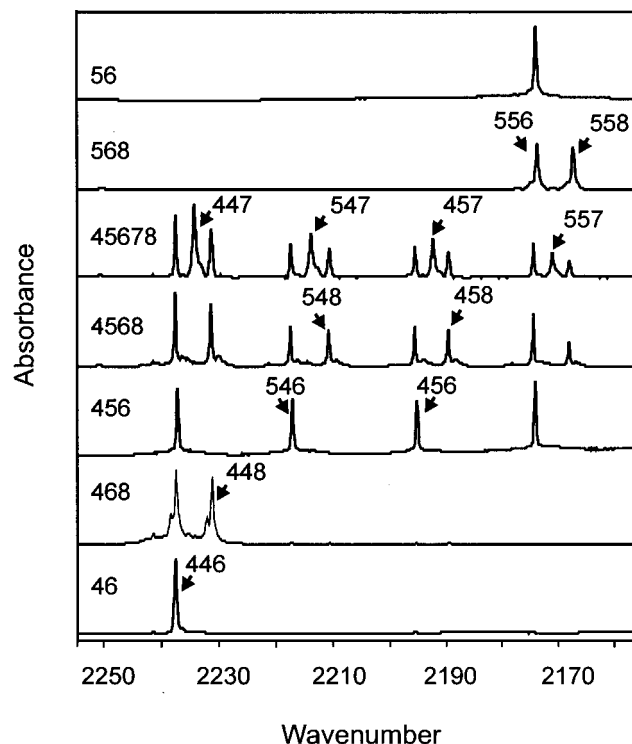


FIG. 1. Portions of IR spectra of N_2O isotopomers in the region of the ν_3 fundamental transition. The spectra were recorded in nitrogen matrices at 10 K. The labeling on the left indicates the isotopic composition of the mixture used in preparing the matrix. For instance, 456 denotes a mixture composed of equal fractions of ^{14}N and ^{15}N ; 4568, a mixture composed of equal fractions of ^{14}N , ^{15}N , ^{16}O , and ^{18}O , and so forth. The symbols labeling individual species indicate their isotopic content, e.g., $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ is labeled 458, and so on.

of the peripheral one, and a small contribution from the oxygen motion. Accordingly, $^{14}\text{N}\rightarrow^{15}\text{N}$ isotopic replacement of a central atom leads to the strongest shift. The observed values for $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{17}\text{O}$, and $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ are $46.8, 46.3$, and 46.0 cm^{-1} , respectively. Similarly, the shifts observed with regard to $^{15}\text{N}^{14}\text{NO}$ as a reference are $47.3, 47.0$, and 46.8 cm^{-1} for $^{15}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{15}\text{N}^{17}\text{O}$, and $^{15}\text{N}^{15}\text{N}^{18}\text{O}$, respectively. Upon substitution of the terminal nitrogen atom, the shifts are about half as large: $22.7, 22.6$, and 22.8 cm^{-1} with respect to $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{17}\text{O}$, and $^{15}\text{N}^{14}\text{N}^{18}\text{O}$, respectively. Taking $^{14}\text{N}^{15}\text{NO}$ as a reference, the corresponding values are $23.2, 23.3$, and 23.6 cm^{-1} for $^{15}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{15}\text{N}^{17}\text{O}$, and $^{15}\text{N}^{15}\text{N}^{18}\text{O}$, respectively. Isotopic substitution of oxygen exerts only a minor effect, with shifts of $3.0\text{--}3.6 \text{ cm}^{-1}$.

The isotopic shifts in the matrix are usually somewhat larger than the corresponding values for the gas phase. This may be caused by a smaller anharmonicity in the solid phase, due to interaction with the environment.

B. ν_1 vibration (Table II and Fig. 2)

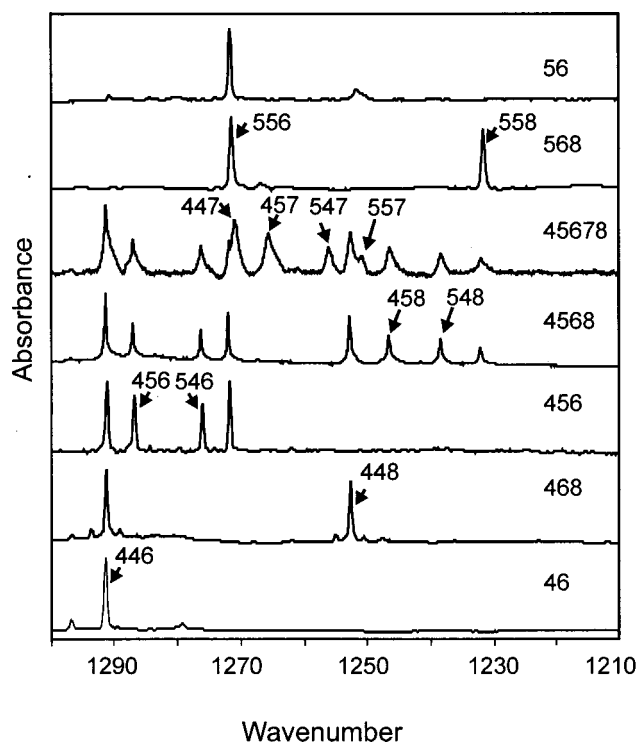
The frequency for the $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ species is 1291.2 cm^{-1} , in excellent agreement with a previously reported value.¹⁰ Similarly as for ν_3 , a blue shift with respect to the gas phase is observed. It is very similar for all species and ranges from 5.4 cm^{-1} for $^{15}\text{N}^{14}\text{N}^{18}\text{O}$ to 6.5 cm^{-1} for

TABLE II. Experimental and calculated frequencies for the ν_1 vibration and the isotopic shifts with respect to parent $^{14}\text{N}^{14}\text{N}^{16}\text{O}$.

	Frequency (cm^{-1})		Isotopic shift (cm^{-1})	
	Experiment ^a	Calculated ^b	Experiment ^a	Calculated ^b
$^{14}\text{N}^{14}\text{N}^{16}\text{O}$	1291.2 (1284.9)	1323.6
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	1276.1 (1269.9)	1301.7	15.1 (15.0)	21.9
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	1286.9 (1280.4)	1321.4	4.3 (4.5)	2.2
$^{15}\text{N}^{15}\text{N}^{16}\text{O}$	1271.7 (1265.3)	1305.3	19.5 (19.6)	18.3
$^{14}\text{N}^{14}\text{N}^{17}\text{O}$	1270.6 (1264.7)	1300.4	20.6 (20.2)	23.2
$^{15}\text{N}^{14}\text{N}^{17}\text{O}$	1255.9 (1250.2)	1284.0	35.3 (34.7)	39.6
$^{14}\text{N}^{15}\text{N}^{17}\text{O}$	1265.4 (1259.3)	1297.8	25.8 (25.6)	25.8
$^{15}\text{N}^{15}\text{N}^{17}\text{O}$	1250.7 (1244.6)	1282.0	40.5 (40.3)	41.6
$^{14}\text{N}^{14}\text{N}^{18}\text{O}$	1252.5 (1246.9)	1279.1	38.7 (38.0)	44.5
$^{15}\text{N}^{14}\text{N}^{18}\text{O}$	1238.3 (1232.9)	1262.8	52.9 (52.0)	60.8
$^{14}\text{N}^{15}\text{N}^{18}\text{O}$	1246.4 (1240.3)	1276.2	44.8 (44.6)	47.4
$^{15}\text{N}^{15}\text{N}^{18}\text{O}$	1231.9 (1226.0)	1260.5	59.3 (58.9)	63.1

^aGas phase values in parentheses (from Refs. 45, 52, 86).^bB3LYP/AUG-cc-pVTZ; see text.

$^{14}\text{N}^{15}\text{N}^{16}\text{O}$. In solid $^{14}\text{N}_2\text{O}$, the blue shift is even larger, the observed value for ν_1 is 1293.4 and that for $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ is 1279.8 cm^{-1} . This is again in contrast to solid argon^{97,100} and xenon,¹⁰¹ where small red shifts of the order of 1–4 cm^{-1}

FIG. 2. Portions of IR spectra of N_2O isotopomers in the region of ν_1 fundamental transition. See caption to Fig. 1 for details.TABLE III. Experimental and calculated frequencies for the ν_2 vibration and the isotopic shifts with respect to parent $^{14}\text{N}^{14}\text{N}^{16}\text{O}$.

	Frequency (cm^{-1})		Isotopic shift (cm^{-1})	
	Experiment ^a	Calculated ^b	Experiment ^a	Calculated ^b
$^{14}\text{N}^{14}\text{N}^{16}\text{O}$	588.0 (588.8)	616.7
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	584.6 (585.3)	613.0	3.4 (3.5)	3.7
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	574.6 (575.4)	602.6	13.4 (13.4)	14.1
$^{15}\text{N}^{15}\text{N}^{16}\text{O}$	571.1 (571.9)	598.9	16.9 (16.9)	17.8
$^{14}\text{N}^{14}\text{N}^{17}\text{O}$	585.5 (586.4)	614.2	2.5 (2.4)	2.5
$^{15}\text{N}^{14}\text{N}^{17}\text{O}$	581.9	610.5	6.1	6.2
$^{14}\text{N}^{15}\text{N}^{17}\text{O}$	572.3	600.0	15.7	16.7
$^{15}\text{N}^{15}\text{N}^{17}\text{O}$	568.4	596.2	19.6	20.6
$^{14}\text{N}^{14}\text{N}^{18}\text{O}$	583.4 (584.2)	611.9	4.6 (4.6)	4.8
$^{15}\text{N}^{14}\text{N}^{18}\text{O}$	580.1 (580.7)	608.2	7.9 (8.1)	8.5
$^{14}\text{N}^{15}\text{N}^{18}\text{O}$	569.9 (570.8)	597.7	18.1 (18.0)	19.0
$^{15}\text{N}^{15}\text{N}^{18}\text{O}$	566.4 (567.2)	593.9	21.6 (21.6)	22.8

^aGas phase values in parentheses (from Refs. 52, 86).^bB3LYP/AUG-cc-pVTZ; see text.

were found. Our data for krypton are consistent with this trend, giving a red shift of about 7 cm^{-1} .

This vibration has been often referred to as N^+-O^- stretching, but the calculated normal mode resembles more a symmetric stretch involving the whole molecule, with the amplitudes of motion of the two terminal atoms much larger than that of the central one. The largest amplitude corresponds to the oxygen atom. Indeed, the most prominent spectral shifts are observed for samples containing oxygen isotopes. $^{16}\text{O} \rightarrow ^{17}\text{O}$ substitution leads to the shifts of 20.6, 20.2, 21.5, and 21.0 cm^{-1} for $^{14}\text{N}^{14}\text{N}^{17}\text{O}$, $^{15}\text{N}^{14}\text{N}^{17}\text{O}$, $^{14}\text{N}^{15}\text{N}^{17}\text{O}$, and $^{15}\text{N}^{15}\text{N}^{17}\text{O}$, respectively. Upon $^{16}\text{O} \rightarrow ^{18}\text{O}$ replacement, the corresponding values are 38.7, 37.8, 40.5, and 39.8 cm^{-1} for $^{14}\text{N}^{14}\text{N}^{18}\text{O}$, $^{15}\text{N}^{14}\text{N}^{18}\text{O}$, $^{14}\text{N}^{15}\text{N}^{18}\text{O}$, and $^{15}\text{N}^{15}\text{N}^{18}\text{O}$, respectively. The shifts accompanying peripheral $^{14}\text{N} \rightarrow ^{15}\text{N}$ substitution are also quite substantial and span a narrow range between 14.2 and 15.2 cm^{-1} . The smallest shifts, 4.3–6.4 cm^{-1} correspond to the $^{14}\text{N} \rightarrow ^{15}\text{N}$ substitution of the central nitrogen atom.

Similarly as in the case of ν_3 , we observe somewhat larger isotopic shifts in the matrix than in the gas phase. Again, this may mean that the vibration becomes more harmonic in the solid environment.

C. ν_2 vibration (Table III and Fig. 3)

The position of the band in a nitrogen matrix is red-shifted by only 0.8 cm^{-1} with respect to the gas phase. In free-standing crystals of xenon the red shift is 4.9 cm^{-1} .¹⁰¹ In argon matrices, a doublet at 589.4 and 588.7 cm^{-1} was observed, and assigned to splitting of the degeneracy of the ν_2 vibration due to a site effect.⁹⁹ We have not detected a similar splitting phenomenon in nitrogen matrices. The degen-

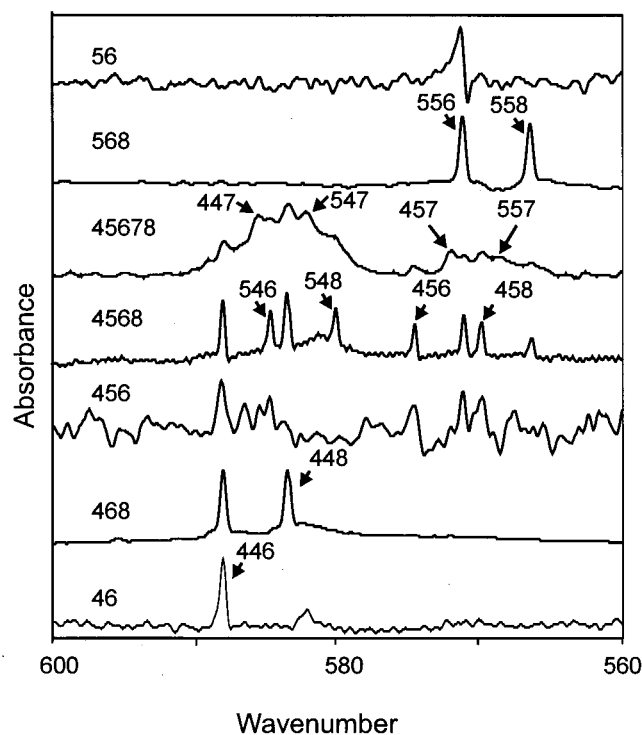


FIG. 3. Portions of IR spectra of N_2O isotopomers in the region of ν_2 fundamental transition. See caption to Fig. 1 for details.

eracy of the ν_2 level is also maintained in solid N_2O .⁹⁵ In the latter case, the reported frequency is 591.0 cm^{-1} , and thus blueshifted with respect to the gas phase, in contrast to all matrix isolation data.

Since ν_2 is a bending vibration, with the largest amplitude of motion exhibited by the central nitrogen atom, the isotopic replacement of the latter should lead to largest shifts. This is indeed the case; the observed values are between 13.2 and 13.7 cm^{-1} . Replacement of a side ^{14}N atom by ^{15}N leads to shifts between 3.3 and 3.9 cm^{-1} . For $^{16}\text{O} \rightarrow ^{17}\text{O}$ and $^{16}\text{O} \rightarrow ^{18}\text{O}$ substitutions, the shifts fall between 2.3 – 2.7 cm^{-1} and 4.5 – 4.7 cm^{-1} , respectively.

Contrary to the cases of ν_1 and ν_3 vibrations, the observed matrix isotopic shifts are practically identical to those in the gas phase, in nice agreement with the observation that the ν_2 vibration is almost harmonic.⁸⁴

D. Combinations and overtones

Tables IV and V contain the frequencies of overtone and combination bands, along with the corresponding gas phase data. These values contribute further evidence for the specific effects exerted by the nitrogen matrix upon the ν_1 and ν_3 stretches. For instance, the blue frequency shifts in N_2 matrix for the first overtones of ν_3 and ν_1 are above 50 cm^{-1} and about 12 cm^{-1} , respectively. In Ar matrices, red shifts of 3 – 4 cm^{-1} were observed for ν_1 ;⁹⁹ in xenon, the red shift is larger, 10.3 cm^{-1} .¹⁰¹ The same is true for combination bands; the gas phase values are bracketed on the blue side by those obtained in nitrogen, and on the red side by those measured in argon or xenon.

TABLE IV. Observed frequencies of the overtone bands.

	Frequency ^a (cm^{-1})			
	$2\nu_1$	$3\nu_1$	$2\nu_2$	$2\nu_3$
$^{14}\text{N}^{14}\text{N}^{16}\text{O}$	2575.3 (2563.3)	3853.7 (3836.4)	1166.6 (1168.1)	4471.6 (4417.4)
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	2546.3 (2534.5)		1158.7 (1160.0)	4426.9 (4373.6)
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	2565.2 (2552.4)		1142.3 (1144.3)	4379.0 (4326.6)
$^{15}\text{N}^{15}\text{N}^{16}\text{O}$	2534.7 (2523.3)		1134.9 (1136.5)	4332.7 (4281.3)
$^{14}\text{N}^{14}\text{N}^{17}\text{O}$	2534.4 (2524.7)		1160.2 (1161.5)	4464.2
$^{15}\text{N}^{14}\text{N}^{17}\text{O}$	2507.8 (2497.1)		1151.9 (1153.0)	4419.2
$^{14}\text{N}^{15}\text{N}^{17}\text{O}$	2523.2 (2511.2)		1135.9 (1138.3)	4371.9
$^{15}\text{N}^{15}\text{N}^{17}\text{O}$	2494.5 (2482.9)		1129.1 (1130.2)	4325.3
$^{14}\text{N}^{14}\text{N}^{18}\text{O}$	2501.4 (2491.2)		1154.1 (1155.1)	4457.5 (4403.0)
$^{15}\text{N}^{14}\text{N}^{18}\text{O}$	2474.7 (2465.0)		1145.5 (1146.2)	4412.1
$^{14}\text{N}^{15}\text{N}^{18}\text{O}$	2486.4 (2474.7)		1128.3 (1132.6)	4366.4
$^{15}\text{N}^{15}\text{N}^{18}\text{O}$	2457.4 (2447.2)		1123.0 (1124.3)	4318.8 (4267.0)

^aGas phase values in parentheses (from Refs. 44, 51–54, 68, 86).

Calculated frequencies for all isotopomers along with the experimental ones are presented in Tables I–III. The agreement is very good, especially when the isotopic shifts are compared. For a particular vibration, the ratio of experimental and calculated frequencies is constant within less than 0.4% along the series of all isotopomers. These ratios vary slightly for the three fundamentals, being 0.977 , 0.953 , and 0.956 for ν_1 , ν_2 , and ν_3 , respectively. Figure 4 presents the correlation between calculated and observed spectral shifts. With the above ratios as scaling factors, the isotopic spectral shifts for ν_1 , ν_2 , and ν_3 could be reproduced with standard deviations of 2.99 , 0.12 , and 1.65 cm^{-1} , respectively. It is worth noticing that the best accuracy was obtained for the ν_2 vibration; it is known that the bending potential is almost harmonic.⁸⁴

IV. SUMMARY AND CONCLUSIONS

Frequencies of fundamental, overtone and combination bands for all 12 isotopomers of N_2O have been obtained and compared with corresponding data for the gas phase and other matrices. Specific influence of the nitrogen matrix upon the shape of the potential energy surface has been discussed, resulting in a blue shift for the frequencies of both stretching vibrations. Since an analogous shift has been observed for solid N_2O ,⁹⁵ one may postulate that the factor responsible for the blue shift has to do with a repulsive character of the N–N interaction potential, contrary to the case of the interactions with argon or xenon. In consequence, ν_1 and ν_3 vibrations become more harmonic in a nitrogen matrix.

Our data may serve as input to further refinement of the force field of nitrous oxide. It was previously attempted to

TABLE V. Observed frequencies of the combination bands.

	Frequency ^a (cm ⁻¹)					
	$\nu_1 + \nu_2$	$\nu_1 + \nu_3$	$\nu_2 + \nu_3$	$\nu_1 + 2\nu_2$	$\nu_1 + 3\nu_2$	$2\nu_2 + \nu_3$
¹⁴ N ¹⁴ N ¹⁶ O	1885.3 (1880.3)	3499.3 (3480.8)	2809.3 (2798.3)	2466.5 (2462.0)	3052.3 (3046.2)	3374.5 (3364.0)
¹⁵ N ¹⁴ N ¹⁶ O		3461.9 (3443.7)	2783.6 (2772.8)	2444.4 (2431.3)		
¹⁴ N ¹⁵ N ¹⁶ O		3450.7 (3432.2)	2750.4 (2739.6)	2435.5		
¹⁵ N ¹⁵ N ¹⁶ O	1847.8 (1842.4)	3411.0 (3394.2)	2723.2 (2713.1)	2413.8		3274.8 (3264.7)
¹⁴ N ¹⁴ N ¹⁷ O		3474.7	2802.5			
¹⁵ N ¹⁴ N ¹⁷ O		3440.4	2777.5			
¹⁴ N ¹⁵ N ¹⁷ O		3425.6	2746.5			
¹⁵ N ¹⁵ N ¹⁷ O		3391.8	2718.5			
¹⁴ N ¹⁴ N ¹⁸ O		3452.7 (3435.0)	2798.2 (2787.0)	2416.5		
¹⁵ N ¹⁴ N ¹⁸ O		3416.2 (3398.4)	2772.1	2393.9		
¹⁴ N ¹⁵ N ¹⁸ O		3403.4 (3385.2)	2739.6 (2728.6)	2385.3		
¹⁵ N ¹⁵ N ¹⁸ O		3363.8 (3347.4)	2711.8 (2701.6)			

^aGas phase values in parentheses (from Refs. 44, 52, 53, 66, 86).

build a force field for the N₂O molecule in the nitrogen matrix cage, basing exclusively on the values of vibrational frequencies measured in a matrix.⁹⁶ Five different N₂O isotopomers were used. However, due to insufficient number of experimental data points (32), the force constants could not be obtained without introducing additional constraints on the potential energy. With over 100 frequency values provided by this work, we believe such an endeavor is now feasible.

Finally, we would like to use our data for a kind of prediction that may be of importance in atmospheric chemistry. It has been postulated that the atmospheric enrichment in some N₂O isotopomers is related to various rates of photolysis of different isotopic species.⁹ This, in turn, should be

due to relatively small shifts in the electronic absorption spectrum of individual isotopomers in the 190–210 nm region. These shifts may be predicted on the basis of ZPE energies. Such an analysis has been previously presented for eight isotopomers.⁹ We have repeated this procedure, adding an additional four species. The results are shown in Fig. 5. It is readily seen that the ¹⁵N¹⁵N¹⁷O and ¹⁵N¹⁵N¹⁸O species should exhibit the largest blue shift. This means that they should be the most difficult to photolyze, and one can therefore expect their presence in the atmosphere in larger than statistically dictated amounts.

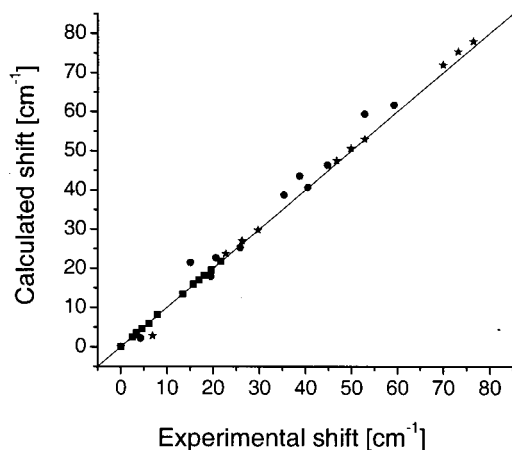


FIG. 4. Correlation between experimental and calculated (B3LYP/AUG-cc-pVTZ) frequency shifts upon isotopic substitution of N₂O. ν_1 , circles; ν_2 , squares; ν_3 , stars. The calculated values have been scaled by the factors of 0.977, 0.953, and 0.956 for ν_1 , ν_2 , and ν_3 , respectively (see text for details).

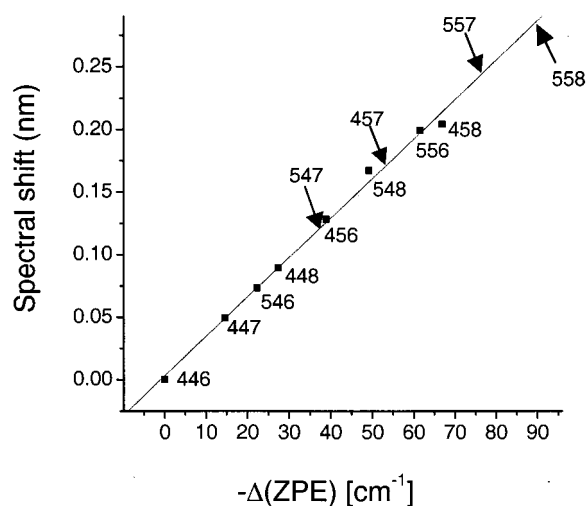


FIG. 5. Correlation between the changes in experimentally determined ZPEs with respect to ¹⁴N₂¹⁶O and the blue shift in the electronic spectrum. The spectral shifts for points indicated by squares were taken from Ref. 9. The arrows indicate predicted shifts for the four remaining isotopomers based on the results of this work.

ACKNOWLEDGMENTS

This project was supported by grants from the NREL DDRD program and from DARPA/AFOSR (F49620-98-1-0483). Part of the instrumentation used in this project was obtained by funds from a DURIP grant.

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