$\tilde{A}~^2E^{\prime\prime}{-}\tilde{X}^2A_2{'}$ Transition of NO3 Trapped in Solid Neon †

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NO₃ has been stabilized in a neon matrix at 4.3 K in sufficient yield for detection of the absorptions between 7000 and 10 000 cm⁻¹, which arise from vibronically allowed transitions from the ground state to levels of the $\tilde{A} {}^{2}E''$ state. The results confirm and somewhat extend previous gas-phase observations for ${}^{14}N^{16}O_{3}$. Additional spectra are presented for six other isotopologues of NO₃, four of which possess C_{2v} symmetry. The splitting patterns for these species support the previous assignments. Alternations in the spacings of the ν_4 progression are consistent with the occurrence of weak to moderate Jahn–Teller interaction in the A 2E state of NO₃.

I. Introduction

The NO₃ free radical is a key participant in atmospheric chemistry.^{1,2} Because most of it results from the reaction of NO₂ with O₃, its formation contributes to upper-atmosphere ozone depletion. During the daytime, NO₃ is readily photodissociated by solar radiation, leaving OH as the primary oxidizing species in the lower atmosphere. However, at night NO₃ becomes the principal oxidant, reacting with a variety of organic molecules to form noxious pollutants such as HNO₃, an important component of acid rain.

 NO_3 is also a benchmark molecule for understanding details of the interaction between molecular electronic energy levels. Eisfeld and Morokuma³ reported the results of CASSCF and MR-SDCI calculations for the ground electronic state of NO_3 and for its excited electronic states up to approximately 100 000 cm⁻¹. Two of these excited electronic states have been observed.

The more familiar is the very prominent visible band system $(\tilde{B}^2E'-\tilde{X}^2A_2')$ with absorptions between about 665 and 480 nm, known for many years but first attributed to NO₃ by Jones and Wulf.⁴ Because of the prominence and distinctive position of the band origin, it has often been used to map the behavior of NO₃ in gas-phase reaction systems. The first high-resolution study of it was attempted by Ramsay.⁵ However, the vibrational bands were found to be broad and unstructured, because of predissociation to form both NO and NO₂. There have been many studies of the details of these two processes, which are also of great concern in atmospheric chemistry.

A new electronic transition of NO₃, $\tilde{A} {}^2E'' - \tilde{X} {}^2A_2'$, was first identified in the photoelectron spectrum of NO₃⁻ by Weaver and co-workers⁶ and later by Wang and co-workers.⁷ Although this transition is optically forbidden, several vibronic transitions have been observed in near-infrared absorption studies. Hirota and co-workers⁸ conducted a high-resolution diode laser study of the band at 7602 cm⁻¹, which was assigned to a transition from the ground vibronic state (²A₂') to the vibronically active ²A₁" level associated with ν_4 of NO₃ ($\tilde{A} {}^2E''$). Shortly thereafter, Kawaguchi and co-workers⁹ detected the vibronically allowed absorption to the $v_2 = 1$ level, leading to the refinement of the position of the band origin to 7061(8) cm⁻¹. Deev and

co-workers¹⁰ obtained evidence for significant Jahn–Teller interaction in their study of the cavity ringdown spectrum of the transition covering the range from 5000 to 9000 cm⁻¹.

There is abundant evidence for the interaction of these two low-lying electronic states of NO3 with each other and with the ground state. Carter and co-workers¹¹ attempted a highresolution study of the B state band origin, which they found to be relatively broad, with several partially resolved maxima. A detailed analysis was not conducted. The analysis by Weaver and co-workers⁶ of the NO₃⁻ photoelectron spectrum included progressions involving single-quantum excitation of v_4 , a degenerate fundamental, of the state of NO₃. A single-mode coupling approach was used to explain this anomaly. Mayer and co-workers12 generalized this approach to multimode coupling, using the model Hamiltonian procedure developed by Köppel and co-workers.¹³ Okumura and co-workers¹⁴ and Stanton and Okumura¹⁵ considered the assignment of the observed absorptions of NO₃ (\tilde{A} ²E") in the light of these preliminary theoretical calculations. Mahapatra and co-workers¹⁶ also attempted to fit the vibronic structure in the photodetachment spectrum of NO3⁻ using a quadratic vibronic coupling approach together with large-scale MRCI calculations.

Many workers have attributed major anomalies in the infrared spectrum of ground-state NO₃ to interaction with the \tilde{B} state. The experimental observations were recently summarized and extended by Jacox and Thompson,¹⁷ who compared the results with those obtained by Stanton^{18,19} in his adaptation of the multimode coupling approach to the ground-state infrared spectrum of NO₃.

There remains considerable room for further experimental studies of transitions to the two lowest excited electronic states of NO₃. Studies of the $\tilde{A}-\tilde{X}$ transition could provide support for the heretofore unique spectroscopic survey by Deev and coworkers,¹⁰ possibly also extending the observed absorption range for this transition. The availability of isotopic substitution data would also be useful in validating theoretical models. Studies of the spectroscopic properties of the isotopologues which have C_{2v} symmetry, for which vibronic degeneracy does not occur, may aid in assessing the role of Jahn–Teller interaction for the results of a detailed study of the infrared spectrum of ground-state NO₃ trapped at 4.3 K in solid neon, conducted at a

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resolution of 0.2 cm^{-1} .¹⁷ Most shifts from the positions of the gas-phase absorption band centers were less than 2.5 cm⁻¹, and all of them were less than 7 cm⁻¹. A new procedure for stabilizing NO₃ in solid neon permitted observation of the infrared spectra of seven isotopologues, and an eighth was observed in lower yield using a discharge sampling procedure. A survey of the spectral region in which the $\tilde{A}-\tilde{X}$ absorption band system of NO₃ was reported by Deev and co-workers showed weak absorptions that could be assigned to seven isotopologues of NO₃. The results of this survey are presented in this paper.

II. Experimental Details²⁰

The NO and O₂ samples and the source of the neon matrix gas were the same as in the earlier study of the ground-state spectra of normal and isotopically enriched NO₃.¹⁷ As before, Ne:NO = 400:1 and Ne:O₂ = 200:1 mole ratios were used for all of the experiments. Because the discharge sampling technique used to produce ¹⁴N¹⁸O₃ for the ground-state studies gave a lower yield than did the simple deposition technique used for most of the studies, no attempts were made to produce that isotopologue for studies of the excited electronic states. To minimize conversion of the NO to NO_2 in the initial deposit, the two mixtures were introduced into the cryogenic cell, also previously described, from separate manifolds. The resulting deposit was warmed to approximately 7 K and recooled to 4.3 K to enhance the probability of NO molecules having O2 molecules as nearest neighbors. The NO₃ absorptions were considerably enhanced by exposing the annealed deposit to medium-pressure mercury arc radiation that had been passed through a filter of Corning glass type 9863, which excludes radiation outside the 240-420 nm spectral region. Filtering of visible light of wavelength shorter than 630 nm from the beam was essential to avoid photodissociation of the NO₃.

The absorption spectra of the sample deposits were obtained using a Bomem DA3.002 Fourier-transform interferometer with transfer optics that have been described previously.²¹ Because the output of the quartz-halogen lamp used for the spectral observations includes considerable visible radiation at wavelengths shorter than approximately 630 nm, to obtain a satisfactory signal-to-noise ratio for the absorptions of NO₃ in its excited electronic states, it was necessary to perform a few cycles of annealing, irradiation through the 240-420 nm bandpass filter, and spectral recording. The spectra taken after each set of procedures were signal-averaged to obtain the final spectrum. Spectra were recorded between 4000 and 12 000 cm⁻¹ at a resolution of 0.2 cm⁻¹, using the quartz-halogen lamp, a quartz beamsplitter optimized for the visible spectral region, and an InSb detector cooled to 77 K. The most prominent absorptions of atmospheric water between 7094 and 7263 cm⁻¹ agreed within 0.1 cm⁻¹ with the positions of these absorptions reported by Toth.22

Selective photodestruction of NO_3 was achieved by exposing the deposit to tungsten-lamp radiation of wavelength longer than 520 nm, obtained using a filter of Corning glass type 3484. In some experiments, the NO_3 was later regenerated using the procedure already described. At the end of the experiment, more extensive, irreversible photodestruction was sometimes induced by exposing the deposit to the unfiltered output of the mediumpressure mercury arc.

III. Results and Discussion

The 7500–9500 cm⁻¹ spectral region, shown for a typical deposit in Figure 1, includes most of the absorptions attributable



Figure 1. NO₃ $\tilde{A}-\tilde{X}$ absorptions. 14.8 mmol Ne:NO = 400 codeposited at 4.3 K over a period of 270 min with 12.1 mmol Ne:O₂ = 200, followed by two periods of warming to 7.4 K, recooling to 4.3 K, and Hg-arc irradiation, 240–420 nm, for 25 min.

to the A-X transition of NO₃. These absorptions appeared on a steeply sloping background, a result of optical scattering of the deposit, which increases considerably at the higher frequencies. Moreover, falloff in the InSb detector response contributed increasing noise at these higher frequencies. To show the weak higher frequency absorptions at a reasonable scale, a linear background correction was applied. The curvature of the resulting plot does not imply underlying continuous absorption, but rather the approximate nature of the background correction. The positions of the sharp, weak absorptions are summarized, together with those of the corresponding absorptions of gasphase NO₃,⁸⁻¹⁰ in the first numerical column of Table 1. Each of the relatively prominent gas-phase absorptions is correlated with a pair of neon-matrix absorptions, typically separated by 23-25 cm⁻¹. The higher frequency absorption of this pair lies less than 10 cm⁻¹ below the gas-phase band center. At the two ends of the spectrum, where the absorptions are weak, there are some exceptions to these generalizations. Results of the isotopic substitution studies are summarized in the remaining columns of Table 1.

Analysis of the NO₃⁻ photoelectron spectrum by Weaver and co-workers⁶ gave estimates of 7000 (1100) cm⁻¹ for the optically inactive origin of the NO₃ $\tilde{A}-\tilde{X}$ transition and of 541(8) cm⁻¹ for the ν_4 fundamental of NO₃ (\tilde{A}). As noted by Kawaguchi and co-workers,⁹ the presumption that the 7602 cm⁻¹ band analyzed by Hirota and co-workers⁸ is contributed by the vibronically active a₁" component of ν_4 permits refinement of the position of the band origin to 7061(8) cm⁻¹. Although absorption at the band origin is vibronically forbidden, Deev and co-workers¹⁰ reported a weak absorption at approximately 7064 cm⁻¹. A very weak absorption also appeared at 7058.5 cm⁻¹ in the present neon-matrix experiments.

The parallel band that appears in the gas phase at 7602 cm⁻¹ has been consistently assigned to v_4 of NO₃ (\tilde{A}).^{8,10} Detail of the neon-matrix NO₃ absorption pattern in this spectral region is shown in Figure 2. The most prominent absorption is at 7578.0 cm⁻¹. That peak has a partly resolved shoulder at 7580.3 cm⁻¹ and a weak satellite at 7584.7 cm⁻¹. Another weak absorption appears at 7601.4 cm⁻¹, very close to the 7602.58 cm⁻¹ gas-phase band center and 23.4 cm⁻¹ higher in frequency than the more prominent peak at 7578.0 cm⁻¹. For a ²E'' electronic state, a vibration of e' symmetry has three vibronic levels: one each of ²A₁'', ²A₂'', and ²E'' symmetry. Of these, absorption from the ground-state ²A₂' vibronic level is allowed only to the upper-state ²A₁'' level, and a parallel band should result. When the molecular symmetry is reduced to $C_{2\nu}$ by partial O-atom isotopic substitution, this ²A₁'' level becomes a ²A₂ level. Moreover, the

TABLE 1:	Positions ((cm^{-1})	and App	proximate	Relative	Intensities ^{<i>a</i>}	Observed	for	Absorptions	between	7000	and	10000	cm ⁻¹	of
Normal and	d Isotopical	lly Sub	stituted	NO ₃											

medium	$^{14}N^{16}O_3$	$^{14}N^{16}O_2^{-18}O_2$	$^{14}\mathrm{N}^{16}\mathrm{O}^{18}\mathrm{O}_2$	¹⁵ N ¹⁶ O ₃	$^{15}N^{16}O_2{}^{18}O$	${}^{15}\mathrm{N}{}^{16}\mathrm{O}{}^{18}\mathrm{O}{}_2$	¹⁵ N ¹⁸ O ₃	assignment
gas ^b	ca. 7064w							0000
Ne matrix	7058.5vw			7055.7vw				
gas ^b	7230w							
$gas^{b,c}$	7602							0001
Ne matrix	7578.0	7568.7	7560.3	7572.2	7563.4	7554.9	7546.3	
	7580.3sh		7563.9	7574.8sh	7567.8	7558.7		
	7584.7w							
	7601.4			7596.2		7578.8w	7570.2w	
$gas^{b,c,d}$	7742(1)							0100
Ne matrix	7714.5	7706.3	7702.7	7694.0	7685.7	7681.5	7684.5	
			7713.5		7694.7	7692.7		
	7739.1	7730.7	7726.9	7718.5	7710.1	7705.9	7709.0	
	110011	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	7738.1	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	7719.3	7717.4	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
$\sigma a s^b$	8121(1)		7750.1		//1).5	//1/.4		0002
Ne matrix	8092.2	8074 7	8057.6	8080.9	8064.0	8047.4	8034.8	0002
ite mauix	8096.1	8070.0	8061.0	8084.8	8068.8	8048 2	8030.0	
	0090.1	0079.0	8001.0	0004.0	0000.0	8040.2 w	0039.0	
	0116 /			Q104 Q		8003W		
aaah	0110.4 9297(2)			0104.0		8071.0W		0101
gas"	8287(3)	0041 7	8220 (0000 1	0210.0	92067	0100.0	0101
Ne matrix	8250.1	8241.7	8229.6	8233.1	8218.9	8206.7	8198.0	
	0001.0	8247.5	8235.7	0057.0	8224.2	8213.0	0000 1	
	8281.0	8266.2	8254.3	8257.9	8243.5	8231.4	8223.1	
L		8272.1	8260.9		8248.9	8237.8		
gas ^{<i>v</i>}	8365(3)							1001
Ne matrix	8311.7vw					8264.6w		
						8270vw		
gas ^b	8527s							1100
Ne matrix	8497			8466w,br		8431w	8431	
	8522			8490vw,br			8454vw,br	
gas ^b	8668(1)							0003
Ne matrix	8637				8623w,br	8576vw	8548.2w	
Ne matrix	8729			8717.1				
Ne matrix	8783.7			8756.2		8720w,br	8698.3	0102
	8809.2			8780.9			8723.3	
gas^b	8900(3)							1002
Ne matrix	8855			8828			8763vw.br	
	8879.6			8853			,-	
	8896 3vw			8872vw		8854w		
Ne matrix	9077.7			9025		00511	8954	1101
i to matrix	<i>J</i> 077117			9051			8979	1101
Ne matrix	9151 72		9107 42	7051			0717	2001
Ne matrix	0342	93212	0208.3	9297		9256	0231	0103
The manix	0365 5	<i>732</i> 1:	0323	0320		9230 9280vvv	02562	0105
No motrix	9303.5		7525	9520		9200VW	92301	0104
ine mauix	2003.3			70101				0104

^{*a*} This work. Based on previous investigations, the standard uncertainty (type B) in the frequency measurement is 0.1 cm⁻¹ (1 σ). Vw = very weak; w = weak; s = strong; br = broad; sh = shoulder. ^{*b*} Reference 10. ^{*c*} Reference 8. ^{*d*} Reference 9.

 ${}^{2}A_{2}'$ ground-state level of the D_{3h} molecule correlates with a ${}^{2}B_{2}$ level for the C_{2v} molecule, from which optical transitions to ${}^{2}A_{1}$, ${}^{2}A_{2}$, and ${}^{2}B_{2}$ levels are allowed. The transition from the ${}^{2}B_{2}$ ground state to the ${}^{2}A_{2}$ vibronic level contributes a single absorption. This is illustrated in Figure 2c, in which the predominant product, ${}^{14}N^{16}O^{18}O_{2}$, has C_{2v} symmetry and there is one major peak at 7560.3 cm⁻¹. In the experiment of Figure 2b, three isotopologues are formed. The absorptions of Figure 2a,c appear weakly, and a new absorption at 7568.7 cm⁻¹ is contributed by ${}^{14}N^{16}O_{2}{}^{18}O$.

For clarity, in the following discussion examples will be drawn from the studies of the oxygen-substituted isotopologues of ¹⁵NO₃, for which it was possible to prepare each of the four isotopologues in separate experiments. All of the results obtained in the experiments on the ¹⁵NO₃ isotopologues are consistent with those obtained in the experiments on the ¹⁴NO₃ isotopologues. The spectra of the ¹⁵NO₃ counterparts of the 7602 cm⁻¹ gas-phase band are shown in Figure 3. The product yields in three of these experiments are sufficiently high to show a very weak or weak absorption about 24 cm⁻¹ above the major one.

As noted by Deev and co-workers,¹⁰ a perpendicular band at 7742 cm⁻¹ possesses ²E' vibronic symmetry. As in the earlier work of Kawaguchi and co-workers,⁹ it is assigned to the ν_2 fundamental, which has a₂" vibrational symmetry and contributes a single level of ²E' vibronic symmetry to the \tilde{A} ²E" state of NO₃. However, when the symmetry of the molecule is reduced to $C_{2\nu}$ by partial ¹⁸O-isotopic substitution, this ²E' level splits into ²A₁ and ²B₂ levels, and absorption to both of these levels is vibronically allowed from the ground ²B₂ state.

Trace a of Figure 4, for ¹⁵N¹⁶O₃, shows a pair of absorptions with approximately equal peak intensities but different contours, separated by 24.5 cm⁻¹. Trace d, for ¹⁵N¹⁸O₃, is similar, with a peak separation of 24.5 cm⁻¹. However, traces b and c, for the two isotopologues which have C_{2v} symmetry, show a doubling of this absorption pattern. The ²A₁ and ²B₂ components of ¹⁵N¹⁶O₂¹⁸O are separated by 9.1 cm⁻¹, and each of these peaks has a counterpart 24.5 cm⁻¹ lower in frequency. Similarly, the two components of ¹⁵N¹⁶O¹⁸O₂ are separated by 11.4 cm⁻¹, and each has a companion absorption approximately 24.5 cm⁻¹ lower



Figure 2. Absorption spectra of ν_4 of normal and ¹⁸O-enriched ¹⁴NO₃ (Ã). (a) See caption to Figure 1. (b) 14.8 mmol Ne:NO = 400 codeposited at 4.3 K over a period of 268 min with 12.4 mmol Ne:O₂ (58% random ¹⁸O enrichment) = 200, followed by seven periods of warming to 7.0 to 7.3 K, recooling to 4.3 K, and Hg-arc irradiation, 240–420 nm, for 20 min. (c) 14.3 mmol Ne:NO = 400 codeposited at 4.3 K over a period of 260 min with 11.9 mmol Ne:¹⁸O₂ = 200, followed by three periods of warming to 6.9 to 7.3 K, recooling to 4.3 K, and Hg-arc irradiation, 240–420 nm, for 20 min.

in frequency. This behavior is consistent with the previously offered assignment of the 7742 cm⁻¹ peak to ν_2 of NO₃ in its \tilde{A} state.

Deev and co-workers¹⁰ assigned a parallel band at 8121 cm⁻¹ to $2\nu_4$ of NO₃ (\tilde{A}). This transition should have a single optically active vibronic level of ²A₁" symmetry. As is shown in Figure 5, each of the four isotopologues related to ¹⁵NO₃ shows a single major absorption, consistent with the previous assignment. In most of these systems a weaker peak appears about 4 cm⁻¹ above this absorption, and in some of the experiments another weak absorption appears about 24 cm⁻¹ above the major absorption.

The most prominent band in the spectrum reported by Deev and co-workers¹⁰ lies at 8287 cm⁻¹. These workers suggested that this absorption might be contributed by v_3 but later recognized²³ that it matches the expected position of the ²E' vibronic level of $v_2 + v_4$. Its counterpart for ¹⁵NO₃ is shown in Figure 6. As was found for v_2 in the neon-matrix experiments the D_{3h} isotopologues each contribute a pair of approximately equally intense absorptions separated by about 25 cm⁻¹. The two levels characteristic of the C_{2v} isotopologues are separated by approximately 6 cm⁻¹.

Deev and co-workers¹⁰ observed another prominent absorption at 8365 cm⁻¹ but were unable to determine its type. They tentatively assigned it to $\nu_1 + \nu_4$, consistent with the values derived for these two fundamental frequencies in the photoelectron spectral studies.⁶ This absorption is very weak in the neon-matrix experiments.

Deev and co-workers¹⁰ assigned a strong perpendicular band at 8527 cm⁻¹ to $\nu_1 + \nu_2$. This absorption is also weak in the neon-matrix experiments, but for the three D_{3h} isotopologues a pair of approximately equally intense peaks separated by approximately 24 cm⁻¹ appeared, consistent with the earlier assignment.



Figure 3. Absorption spectra of ν_4 of ${}^{15}NO_3$ (\tilde{A}) and its ${}^{18}O$ -enriched isotopologues. (a) 13.8 mmol Ne:¹⁵NO = 400 codeposited at 4.3 K over a period of 255 min with 11.6 mmol Ne: $O_2 = 200$, followed by an initial 20 min 240-420 nm Hg-arc irradiation, then by three periods of warming to 6.8-7.2 K, recooling to 4.3 K, and Hg-arc irradiation, 240-420 nm, for 20 min. (b) 13.9 mmol Ne:¹⁵N¹⁸O = 400 codeposited at 4.3 K over a period of 261 min with 11.9 mmol Ne: $O_2 = 200$, followed by an initial 20 min 240-420 nm Hg-arc irradiation, then by three periods of warming to 7.0-7.3 K, recooling to 4.3 K, and Hgarc irradiation, 240-420 nm, for 20 min. (c) 13.3 mmol Ne:¹⁵NO = 400 codeposited at 4.3 K over a period of 247 min with 11.3 mmol Ne:¹⁸O₂ = 200, followed by an initial 20 min 240–420 nm Hg-arc irradiation, then by three periods of warming to 6.7-7.2 K, recooling to 4.3 K, and Hg-arc irradiation, 240-420 nm, for 20 min. (d) 13.5 mmol Ne: ${}^{15}N^{18}O = 400$ codeposited at 4.3 K over a period of 261 min with 11.8 mmol Ne: ${}^{18}O_2 = 200$, followed by an initial 20 min 240-420 nm Hg-arc irradiation, warming to 7.3 K, recooling to 4.3 K, and another 20 min 240-420 nm Hg-arc irradiation.



Figure 4. Absorption spectra of ν_2 of ¹⁵NO₃ (\tilde{A}) and its ¹⁸O-enriched isotopologues. (a)–(d) See Figure 3.

A parallel band which appeared at 8668 cm⁻¹ in the gasphase spectrum¹⁰ was assigned to $3\nu_4$. In the neon-matrix observations on ¹⁴N¹⁶O₃, a single weak absorption was observed at 8637 cm⁻¹. Absorptions of the other isotopologues were weak or very weak.



Figure 5. Absorption spectra of $2\nu_4$ of ${}^{15}NO_3$ (\tilde{A}) and its ${}^{18}O$ -enriched isotopologues. (a)–(d) See Figure 3.



Figure 6. Absorption spectra of $\nu_2 + \nu_4$ of ¹⁵NO₃ ($\tilde{\mathbf{A}}$) and its ¹⁸O-enriched isotopologues. (a)–(d) See Figure 3.

All of the peaks at higher frequencies except for the very weak neon-matrix absorption at 8729 cm⁻¹ can be placed into two arrays involving excitation of various numbers of quanta of ν_2 and ν_4 or of these same vibrations together with a single quantum of ν_1 , shown in Tables 2 and 3, respectively. The resulting assignments assume that anharmonic contributions are small. A pair of absorptions at 8783.7 and 8809.2 cm⁻¹ in the neon-matrix experiments are separated by 25.5 cm^{-1} . The position of these two absorptions is appropriate for their assignment to $v_2 + 2v_4$. Like the lower frequency absorptions to which ν_2 contributes, they are approximately equally intense. Deev and co-workers¹⁰ observed a band at 8900 cm⁻¹, but its type was uncertain. It was tentatively assigned to $\nu_1 + 2\nu_4$. A similar assignment is proposed in Table 3. Table 1 includes five previously unreported absorptions between 9000 and 9900 cm⁻¹, all of which are relatively weak and appear on a noisy background. Their positions are consistent with the assignments proposed in Tables 2 and 3. The absorptions at 9342 and 9365.5

TABLE 2: Absorptions^{*a*} Observed for NO₃ (\tilde{A} ²E^{''}) for Which ν_2 Is Not Excited, Assigned to Peaks with ²A₁^{''} Vibronic Symmetry

	$v_1=0$		$v_1 = 1$	$v_1=2$
$v_4 = 0$	7064 w			
	7058.5vw			
	538			
$v_4 = 1$	7602	763	8365	
	7578.0	733.7	8311.7vw	9151.7 ?
	7601.4			
	519		535	
	514.2			
	515.0			
$v_4 = 2$	8121	779	8900	
	8092.2	762.8	8855	
	8116.4	763.2	8879.6	
	547			
	545			
$v_4 = 3$	8668			
	8637			

 a Gas-phase values $^{8-10}$ in boldface; other absorptions, Ne matrix, this work. Frequency differences between adjacent levels are shown in italics.

TABLE 3: Absorptions^{*a*} Observed for NO₃ (\tilde{A} ²E^{''}) for Which One Quantum of v_2 Is Excited, Assigned to Peaks with ²E' Vibronic Symmetry

	$v_1 = 0$		$v_1 = 1$
$v_4 = 0$	7742	785	8527
	7714.5	783.1	8497.6
	7739.1	782.5	8521.6
	545		
$v_4 = 1$	8287		9077.7
	8256.1		
	8281.0		
	527.6		
	528.2		
$v_4 = 2$	8783.7		
	8809.2		
	557.9		
	556.3		
$v_4 = 3$	9341.6		
	9365.5		
	542		
$v_4 = 4$	9883.5		

^{*a*} Gas-phase values^{9,10} in boldface; other absorptions, Ne matrix, this work. Frequency differences between adjacent levels are shown in italics.

cm⁻¹ are sufficiently prominent that their counterparts are seen in observations of the spectra of ${}^{15}N^{16}O_3$ and ${}^{15}N^{18}O_3$, as well. In all three systems, these absorptions are separated by 24 cm⁻¹, supporting their assignment to $\nu_2 + 3\nu_4$.

For NO₃ excited to a state of ²E" symmetry, ν_3 and ν_4 are subject to the Jahn–Teller effect. One consequence of this is that excitations of single quanta of these two fundamentals may occur. There are two conflicting assessments of the magnitude of Jahn–Teller distortion for the ²E" state of NO₃. Analysis of the ν_4 band in the high-resolution diode laser studies⁸ suggested that the D_{3h} symmetry of the molecule is retained, consistent with weak vibronic interactions. In contrast, high-level ab initio calculations by Eisfeld and Morokuma³ suggested that significant Jahn–Teller distortion occurs, with the ²B₁ minimum approximately 2000 cm⁻¹ below the conical intersection. Their MR-SDCI calculations indicated that the positions of all of the vibrational fundamentals except possibly ν_2 are widely separated for the two isomers. This prediction is inconsistent with the

TABLE 4: Dependence of Vibrational Spacings cm⁻¹ of Ne-Matrix Progression in v_4 of the $\tilde{A}-\tilde{X}$ Transition of NO₃ on Isotopic Substitution^{*a*}

	$^{14}N^{16}O_3$	$^{15}N^{16}O_3$	$^{15}N^{18}O_3$
	(a) $v_1 = 0, v_2 =$	$= 0, v_3 = 0$	
$\Delta v_4 = 1 - 0$	538		
$\Delta v_4 = 2 - 1$	519		
	514.2	508.7	488.5
	515.0		
$\Delta v_4 = 3 - 2$	547		
	545	542	513.4
	(b) $v_1 = 0, v_2 =$	= 1, $v_3 = 0$	
$\Delta v_4 = 1 - 0$	545		
	541.6	539.1	513.5
$\Delta v_4 = 2 - 1$	527.6	523.1	500.3
$\Delta v_4 = 3{-}2$	557.9	540.8	533

^a Gas-phase separations in boldface.

results of the high-resolution analysis of ν_4 . Okumura and coworkers¹⁴ noted the irregular spacing of the absorptions attributed to a progression in single quanta of ν_4 , all of which have a perpendicular band structure. As is shown in Tables 2 and 3, these irregularities persist in the neon-matrix observations. Moreover, as is shown in Table 4, they are also evident in the observations on ¹⁵N¹⁶O₃ and ¹⁵N¹⁸O₃. As noted by Ramsay⁵ and discussed by Longuet-Higgins and co-workers²⁴ and by Herzberg,²⁵ these irregular spacings, alternating large and small, are consistent with the occurrence of Jahn–Teller interactions. However, all of the experiments suggest that this interaction is weak to moderate in magnitude.

It has been noted that almost all of the $\tilde{A}-\tilde{X}$ absorptions of NO₃ trapped in solid neon have two components separated by approximately 24 cm⁻¹. The two absorptions of transitions involving excitation of v_2 are nearly equally intense, while for other transitions that do not involve ν_2 usually the lower frequency peak is more prominent and the higher frequency peak is sharper and lies close to the gas-phase band. Such differences could arise either from a property of the individual molecule or from the occurrence of molecular interactions. Distortion of the molecule to C_{3v} symmetry would give rise to inversion splitting. The approximately 24 cm⁻¹ observed splitting is close to that observed for NH3 trapped in an argon or a neon matrix.²⁶ For a heavy-atom molecule, such a large splitting would be exceptionally high. Rotation of small molecules, including NH₃, sometimes occurs in rare-gas matrices, but a rotational interval of 24 cm⁻¹ would be much too large for NO₃. Either Jahn-Teller distortion of NO₃ in the à state or partial ¹⁸O substitution would result in a C_{2v} structure. As is illustrated by traces b and c of Figures 4 and 6, each isotopologue with C_{2v} symmetry retains this characteristic 24 cm⁻¹ splitting.

Molecular interaction with the neon matrix and/or with other species in the system may also contribute to this splitting. In the earlier study of the infrared spectrum of ground-state NO₃,¹⁷ almost all of the absorptions involving in-plane vibrations of NO₃ were split, with a weaker satellite absorption 2 or 3 cm⁻¹ above the major peak. The growth in the satellite absorption when the deposit was warmed slightly suggested that this satellite absorption arose from the trapping of NO₃ in sites in which it was weakly perturbed by the presence of a nearby molecule of unreacted NO or O₂. However, a similar study of the behavior of the NO₃ $\tilde{A}-\tilde{X}$ absorptions on mild warming of the deposit showed no change in the relative intensities of the pairs of absorptions. Therefore, it is probable that the splitting arises from the trapping of molecules in sites which offer distinct types of interaction with the face-centered cubic neon lattice. Recently, Stanton and Okumura¹⁵ noted that NO₃ (\tilde{A}) ν_4 and its overtones possess a vibronically active sublevel of ²A₁" symmetry. However, the only low-energy NO₃ vibronic level that has both that vibronic symmetry and an appreciable absorption intensity is ν_2 (a₂") of the ground ²A₂' state. On the other hand, the NO₃ (\tilde{A}) state vibronic levels assigned to transitions in which one quantum of ν_2 is excited have a sublevel of ²E' symmetry, which borrows most of its intensity from the very strongly absorbing NO₃ (\tilde{B} ²E') state. It would not be surprising for transitions with such different coupling mechanisms to have different contours when the molecule is trapped in two or more distinct types of site in solid neon.

In their initial assignment of the structure of the NO₃ (\tilde{A}) band system in the photoelectron spectrum of NO₃⁻, Weaver and co-workers⁶ presumed that bands in which ν_1 (a₁') participated were present and derived a value of 804(4) cm⁻¹ for that fundamental frequency of NO_3 (Å). That assignment was adopted by later workers and is used in Tables 1-3 of this paper. However, recent calculations of the photodetachment spectrum of NO₃⁻ by Mahapatra and co-workers¹⁶ suggested that these bands might instead be contributed by v_3 . In principle, comparison of the positions of transitions of ¹⁴N¹⁶O₃ and ¹⁵N¹⁶O₃ involving excitation of this fundamental should distinguish between the two possible assignments; for v_1 the difference between the two fundamental frequencies should equal zero, whereas for ν_3 it should be large compared to the resolution used for the observations. Because absorption at the band origin is vibronically forbidden, the fundamental frequencies for each of the two isotopologues were derived by obtaining differences between the positions of pairs of combination bands. While complications from zero-point energy differences for the two isotopologues are avoided, the procedure assumes a harmonic vibrational potential function-a severe approximation for a transition known to involve strong vibronic interactions. From the data summarized in Table 1, for ¹⁴NO₃ the (1002)-(0002) band separation equals 780 cm^{-1} and the (1100)–(0100) band separation equals 783 cm⁻¹. In contrast, for ¹⁵NO₃ these two band separations equal 767 and 771.5 cm⁻¹, respectively. Therefore, in this approximation the nitrogen-isotopic dependence in the fundamental amounts to 12 or 13 cm⁻¹. While this difference would be consistent with the proposed reassignment, because of the serious approximation noted above it is not definitive.

IV. Conclusions

The absorption spectrum of the $\tilde{A}-\tilde{X}$ transition of ${}^{14}N^{16}O_3$ reported by Deev and co-workers¹⁰ has been confirmed and somewhat extended by the present neon-matrix study of this band system. Extensive observations of this transition for a total of seven isotopologues of NO₃ are reported. Pairs of absorptions separated by 24 cm⁻¹ appear for all but the weakest transitions. The origin of this splitting is incompletely understood but is likely to involve interactions between NO₃ and neon atoms in the solid. The most developed progressions involve excitation of ν_4 , based on $\nu_2 = 0$ or 1, but a few absorptions involving ν_1 excitation also appear. Alternating large and small spacings in the ν_4 progressions suggest weak to moderate Jahn–Teller interactions.

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(20) Certain commercial instruments and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

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