

The intermolecular vibrations of the NO dimer

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The far infrared spectrum of the NO dimer in the gas phase has been observed for the first time, using a low temperature (100 K) long-path (180 m) absorption cell. The spectroscopic results are used, together with mid-infrared observations and high level CCSD(T) *ab initio* calculations, to locate the four low frequency intermolecular vibrational modes of (NO)₂: ν_2 (symmetric bend)=239.361 cm⁻¹, ν_3 (intermolecular stretch)=134.503 cm⁻¹, ν_4 (out-of-plane torsion)≈117 cm⁻¹, and ν_6 (antisymmetric bend)=429.140 cm⁻¹. These values agree poorly with previous determinations based on condensed-phase spectra, indicating that there are large shifts in going from the isolated gas-phase dimer to the liquid, solid, or matrix-isolated environments. © 1998 American Institute of Physics. [S0021-9606(98)02235-1]

I. INTRODUCTION

Nitric oxide plays a major role in the atmospheric, surface, and biological sciences; interactions among NO radicals are thus of fundamental and practical importance. The propensity of NO to form dimers, (NO)₂, has long been known, but there are still a number of mysteries surrounding this rather basic molecule. A solution of some of these mysteries is the subject of this paper.

The binding energy of the NO dimer is known¹⁻⁴ to be approximately 700 cm⁻¹, an amount that is larger than a normal van der Waals interaction, but, of course, very much smaller than a normal chemical bond. High-resolution gas-phase microwave⁵⁻⁷ and infrared^{3,4,8-10} spectroscopy indicate that the NO dimer has a singlet ground electronic state and a *cis* structure with C_{2v} symmetry, a N–O bond length close to that of the monomer (1.15 vs 1.14 Å), a N–N bond length of 2.26 Å, and a N–N–O angle of 97°. The ν_1 (*a*₁ symmetric) and ν_5 (*b*₂ antisymmetric) N–O stretching bands of (NO)₂ have been unambiguously located by gas-phase spectroscopy at 1868.25 and 1789.10 cm⁻¹, respectively. The four remaining fundamental vibrations occur at much lower frequencies, corresponding to far infrared wavelengths, but they have never previously been observed in the gas phase. However, since nitric oxide in its condensed phases is made up to some extent of dimers, these vibrations have been extensively studied by infrared and Raman spectroscopy in liquid, solid, and matrix-isolated NO.¹¹⁻¹⁶ These studies have not always agreed about the correct locations and assignment of the low frequency modes, but the generally accepted values are probably those given by Nour *et al.*¹⁵ and Menoux *et al.*¹⁷

We have recently made the first gas-phase observations of the weak far-infrared spectrum of the NO dimer, and have also recorded the mid-infrared spectrum with greater detail and accuracy than previously accomplished. In the present paper, we address the mystery of the intermolecular modes of (NO)₂ by employing these data together with results from a new high-level *ab initio* calculation. The spectra result in

definitive assignments of the three infrared-allowed low-frequency fundamental vibrations; ν_2 (*a*₁ symmetric bend), ν_3 (*a*₁ van der Waals stretch), ν_6 (*b*₂ antisymmetric bend). We also locate the remaining IR-forbidden mode, ν_4 (*a*₂ out-of-plane torsion), with reasonable certainty on the basis of mid-infrared observations and theoretical considerations. Our new values for the intermolecular frequencies agree only poorly with the accepted condensed phase values,¹⁵⁻¹⁷ suggesting that (NO)₂ undergoes large vibrational frequency shifts in going from the gas phase to the liquid, solid, or matrix-isolated environments.

II. EXPERIMENT

Most spectra were recorded with the same 5 m low-temperature, long-path, absorption cell and Bomem DA3.002 FTIR spectrometer used previously^{9,10} to study (NO)₂. Modifications for operation in the 200–500 cm⁻¹ region included fitting the cell with polypropylene windows and the spectrometer with a Mylar beamsplitter and either a 4.2 K Cu:Ge photoconductive detector (>320 cm⁻¹) or a 1.6 K Si bolometer detector. Absorption paths were in the range of 140–200 m, corresponding to 28–40 passes of the cell. Sample pressures of up to 22 Torr of NO were used; to put these in perspective, it should be noted that we could easily observe the ν_1 band of (NO)₂ at only 0.6 Torr, and that the concentration of dimers varies approximately as the square of the pressure. The sample temperatures were in a range around 100 K, close to the lowest values possible for the particular pressures used; in other words, the temperature was determined by the vapor pressure of nitric oxide. One spectrum, covering the 100–200 cm⁻¹ region, was recorded with a 2 m cell, using a path of 80 m, a pressure of 35 Torr, and a temperature of 115 K.

The NO samples were purified by passing the gas through a cold trap at –90 °C before entering the absorption cell. In the spectral regions of interest here, absorptions by impurity molecules were not a problem, but we did note the presence of CH₄ and N₂O impurities in the 1200–1400 cm⁻¹

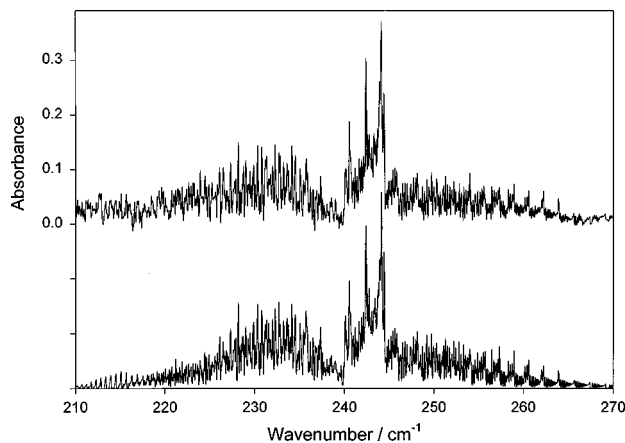


FIG. 1. Observed (upper) and calculated (lower) ν_2 fundamental band spectra of $(\text{NO})_2$, with an absorption path of 140 m, a pressure of 12 Torr, and a temperature of 98 K. The experimental spectral resolution was 0.02 cm^{-1} , but here this is degraded to 0.08 cm^{-1} for clarity.

region. Many other potential impurity molecules would, of course, have a negligible vapor pressure at our low sample temperatures.

III. SPECTROSCOPIC RESULTS

The first, and strongest, new far-infrared band of $(\text{NO})_2$ that we observed is shown in Fig. 1. Even though this band, located around 240 cm^{-1} , turned out to be the strongest low frequency band of the dimer, it is still at least 100 times weaker than the previously known ν_1 and ν_5 N–O stretching bands around 1800 cm^{-1} . Inspection indicated that this was a type-*b* band, like ν_1 , involving an upper state of a_1 symmetry, and we assign it as the ν_2 fundamental because ν_3 was subsequently located at a lower frequency. Since we have precise knowledge⁷ of the rotational levels in the ground vibrational state of $(\text{NO})_2$ and previous experience³ with the ν_1 band, the analysis of ν_2 was relatively straightforward. Ultimately, we made a detailed line-by-line analysis,¹⁸ assigning over 200 lines to transitions with $J \leq 30$ and $K_a \leq 16$, and fitting these with a standard deviation of about 0.0006 cm^{-1} . We thus obtained a complete set of upper state rotational and quartic centrifugal distortion parameters, and determined the ν_2 band origin to be 239.3605 cm^{-1} .

The next vibration that we analyzed was ν_3 , the remaining totally symmetric (a_1) mode of $(\text{NO})_2$. This mode is readily apparent from a type-*a* difference band, $\nu_5 \leftarrow \nu_3$, appearing in the $1650\text{--}1675 \text{ cm}^{-1}$ region as shown in Fig. 2. Fragments of the ν_3 fundamental band are observed in the $130\text{--}160 \text{ cm}^{-1}$ region between lines of the ${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$ monomer band. As shown in Fig. 2, our analysis explains moderately sharp (0.5 cm^{-1}) features at 1651.7 and 1654.8 cm^{-1} as being due, respectively, to the *P*- and *Q*-branches of the $\nu_5 \leftarrow \nu_3$ band. Originally,¹⁰ we assigned the peak at 1651.7 cm^{-1} as the central peak of the type-*c* band $\nu_5 \leftarrow \nu_4$, but the higher pressure spectrum obtained here shows that this band has a similar appearance to the much weaker $\nu_5 \leftarrow \nu_2$ type-*b* band observed near 1550 cm^{-1} (shown in the inset to Fig. 2). The somewhat unusual shapes of these dif-

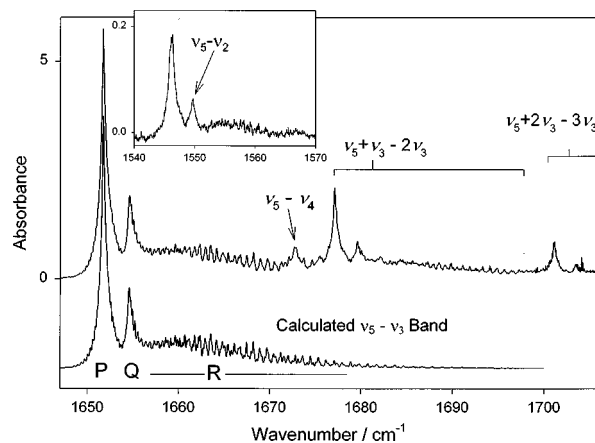


FIG. 2. Observed (upper trace) spectrum of the NO dimer recorded with path=180 m, pressure=22 Torr, and temperature=99 K. The most prominent observed features are due to the $\nu_5 \leftarrow \nu_3$ difference band, which is calculated in the lower trace. The inset shows the much weaker observed spectrum of the $\nu_5 \leftarrow \nu_2$ difference band near 1550 cm^{-1} .

ference bands arise because of relatively large changes in the *B* and *C* rotational constants for the ν_2 and ν_3 states relative to ν_5 (see below).

There is extensive and detailed agreement between the observed and calculated spectra for the $\nu_5 \leftarrow \nu_3$ band from 1650 to 1670 cm^{-1} as shown in Fig. 2. Other features observed in Fig. 2 at 1677 and 1701 cm^{-1} can be explained as due to analogous “piled-up” *P*-branch heads of sequence bands built on $\nu_5 \leftarrow \nu_3$, namely, $\nu_5 + \nu_3 \leftarrow 2\nu_3$ and $\nu_5 + 2\nu_3 \leftarrow 3\nu_3$. The relative intensities in such a sequence are expected to be approximately proportional to $n \exp(-hc\nu_3/kT)$ for the $\nu_5 + (n-1)\nu_3 \leftarrow n\nu_3$ sequence band, and this agrees well with the observed intensities for the sample temperature of 99 K. Various of these 1652 , 1655 , 1677 , and 1701 cm^{-1} features have been observed weakly in previous experiments,^{10,17,19} but no meaningful assignment has been possible until now.

The ν_3 state band origin and rotational parameters are mainly based on line assignments in the type-*b* fundamental ν_3 band around 140 cm^{-1} . Figure 3 shows the extent of obscuration by the considerably stronger NO monomer lines arising from the ${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$ magnetic dipole spin transition.²⁰ Nevertheless, the clear *Q*-branch peak at 138.37 cm^{-1} , as well as some individual resolved ν_3 band lines in the 142 , 145 , and 149 cm^{-1} regions can be seen. The complete calculated ν_3 fundamental band at 115 K is shown in Fig. 4; note the general similarity to the ν_2 band in Fig. 1.

The successful assignment of ν_2 and ν_3 left ν_6 , the b_2 antisymmetric bending vibration, as the remaining unlocated infrared-allowed mode. For this fundamental band, one expects a type-*a* parallel band structure, similar to that of the ν_5 band¹⁰ at 1789 cm^{-1} . Finding this band was difficult because of its extreme weakness. With some theoretical guidance indicating that ν_6 should lie above the other fundamentals (see below), it was ultimately detected in the 430 cm^{-1} region, as shown in Fig. 5. We have made a partial line assignment and fit for this band, but there seem to be some perturbations of the upper state. Our band profile calculation, shown in the lower trace of Fig. 5, shows good, but not perfect, agreement

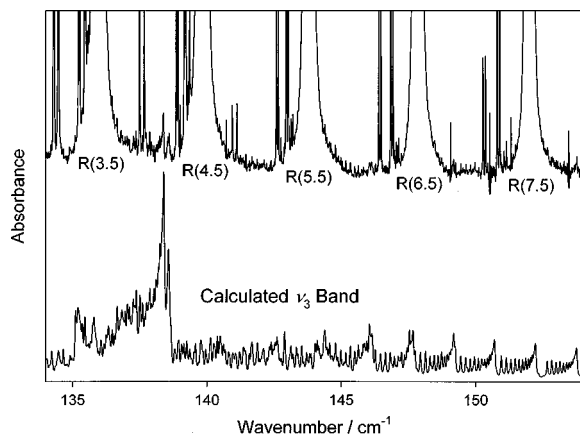


FIG. 3. Observed (upper) and calculated ν_3 fundamental band of $(\text{NO})_2$, with an absorption path of 80 m, a pressure of 35 Torr, and a temperature of 115 K. The upper trace is dominated by the much stronger $R(3.5)$ – $R(7.5)$ lines of the ${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$ electronic transition of the NO monomer (including those of ${}^{15}\text{N}{}^{16}\text{O}$ and ${}^{14}\text{N}{}^{18}\text{O}$).

with the observation; small discrepancies may be due to the perturbations noted, and also due to centrifugal distortion effects. The presence of perturbations is not surprising because ν_6 lies close to $4\nu_4$, $4\nu_3$, and $2\nu_2$, and therefore quite a large number of overtone and combination vibrational states could be perturbing its rotational structure. A somewhat stronger band with type-*b* structure (not shown here) was observed near 350 cm^{-1} ; we assign this as the $\nu_2 + \nu_3$ combination band.

The location of the infrared-forbidden ν_4 vibration (a_2 out-of-plane torsion) was not immediately straightforward from our results. However, guided by our force-field calculations, we assigned a feature observed at 1672 cm^{-1} to the type-*c* $\nu_5 \leftarrow \nu_4$ difference band, and therefore obtained a value of $\nu_4 = 117\text{ cm}^{-1}$; more details are given in Sec. VI below. We have not attempted to make a detailed band profile analysis of the 1672 cm^{-1} feature, since it is overlapped by the stronger $\nu_5 \leftarrow \nu_3$ band, and so we obtained no information on the rotational parameters for the ν_4 state.

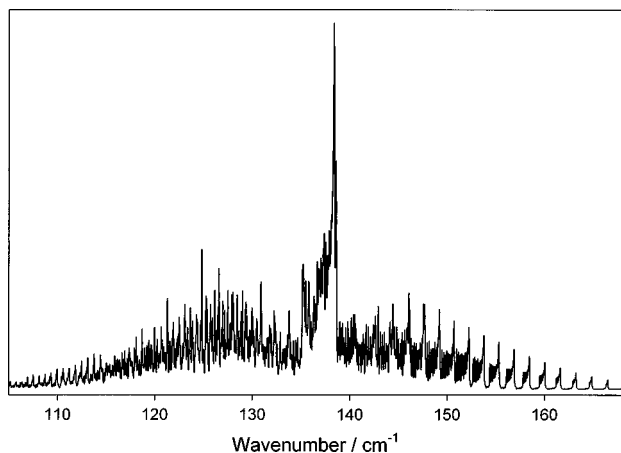


FIG. 4. The calculated spectrum of the ν_2 fundamental band of $(\text{NO})_2$ at 115 K.

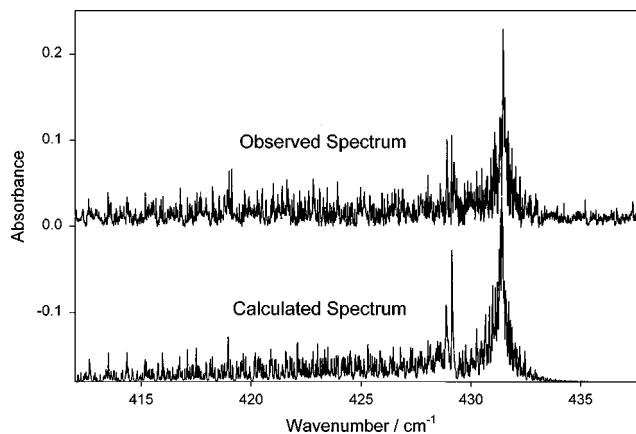


FIG. 5. Observed (upper) and calculated (lower) ν_6 fundamental band spectra of $(\text{NO})_2$, with experimental conditions as in Fig. 2. The prominent feature near 432 cm^{-1} is due to the ‘‘piled-up’’ *R*-branch. *Q*-branch features are evident near 429 cm^{-1} .

The results that we obtained for the intermolecular frequencies of $(\text{NO})_2$ are listed in Table I, where they are compared with previous condensed phase values¹⁵ and a recent Ar matrix isolation study.¹⁶ There are large differences; our ν_2 and ν_3 values are much lower than these previous values, our ν_4 is slightly higher, and our ν_6 is almost double. It is interesting that an Ar matrix band is observed¹⁶ at 243 cm^{-1} , very close to our assignment of ν_2 at 239 cm^{-1} . However, this 243 cm^{-1} band was assigned as ν_6 , while a matrix band at 299 cm^{-1} was assigned as ν_2 .¹⁶ The fractional isotope shift in ν_6 can be calculated from the Teller–Redlich product rule²¹ using the known rotational constants and the observed ν'_5/ν_5 ratio. For the observed ν_5 ratio¹⁶ in an Ar matrix, the ν_6 shift is calculated to be -1.94% for $({}^{15}\text{N}{}^{16}\text{O})_2$. The only far infrared Ar matrix bands with approximately this shift are at 362.4 cm^{-1} in $({}^{14}\text{N}{}^{16}\text{O})_2$ and 355.2 cm^{-1} in $({}^{15}\text{N}{}^{16}\text{O})_2$, giving -1.99% . The other information from the product rule is that for ν_2 and ν_3 the sum of the fractional shifts should be -3.42% , using the observed Ar matrix ν'_1/ν_1 ratio. Unfortunately, it does not seem possible to assign the far infrared observed bands¹⁶ to meet this requirement.

The observed changes in rotational parameters for the intermolecular modes of $(\text{NO})_2$ are listed in Table II, which also gives values^{7,10} for the intramolecular modes, ν_1 and ν_5 . The changes in the *B* and *C* rotational constants upon

TABLE I. Measured frequencies for the intermolecular modes of the NO dimer (in cm^{-1}).

Vibration		Gas phase, Present value	Condensed phases, Ref. 15	Matrix isolation, Ref. 16
$\nu_2(a_1)$	Symmetric bend	239.361	268	299.3
$\nu_3(a_1)$	van der Waals stretch	134.503	189	175.5
$\nu_4(a_2)$	Torsion (IR forbidden)	117	97	103.4
$\nu_6(b_2)$	Antisymmetric bend	429.140	215	242.8

TABLE II. Changes in rotational constants with vibrational excitation for the NO dimer.

Vibration	Vibrational origin/cm ⁻¹	ΔA /MHz	ΔB /MHz	ΔC /MHz
$\nu_1(a_1)^a$	1868.252	-123	+17	+8
$\nu_5(b_2)^b$	1789.098	-138	+106	+67
$\nu_2(a_1)$	239.361	+183	-147	-137
$\nu_3(a_1)$	134.503	-5	-244	-174
$\nu_6(b_2)$	429.140	+41	-423	-289

^aBrookes *et al.* (Ref. 7).^bWatson and McKellar (Ref. 10).

vibrational excitation are considerably larger for the intermolecular than for the intramolecular modes, which is not surprising since the former tend to involve larger amplitude motions. The fact that ν_2 involves a large increase (183 MHz) in the A constant, whereas ν_3 involves little change (-5 MHz), helps to confirm their description as the symmetric bending and van der Waals stretching motions, respectively.

IV. AB INITIO CALCULATIONS

We performed *ab initio* force field calculations to provide initial guidance for our experiments and further insight into the vibrational dynamics of (NO)₂. We chose CCSD(T) theory^{22,23} with the aug-cc-pVDZ basis set²⁴ for the computation of the harmonic force field because it predicts a reasonably accurate geometry for the dimer ($r_{\text{NN}}=2.227$ Å, $r_{\text{NO}}=1.169$ Å, $\theta_{\text{NNO}}=96.2^\circ$).²⁵ The force field and harmonic frequencies were computed from finite difference second derivatives of total energy (with displacements of 0.005 Å and 0.01 rad), using energies computed with MOLPRO (Ref. 26) and coordinate transformations from INTDER.²⁷

Observed and calculated vibrational frequencies are compared in Table III, and the *ab initio* force field is given in Table IV. Overall, it is significant and encouraging that the relative ordering, and approximate magnitude, of the *ab initio* calculations agree well with the present experimental values. In particular, the *ab initio* results favor a significantly higher value for ν_6 than previously proposed.¹⁵⁻¹⁷ The present level of theory predicts r_{NN} to be 0.036 Å too short compared to experiment,⁹ and r_{NO} to be 0.018 Å too long, thus implying a dimer which is slightly too tightly bound. This suggests that the *ab initio* harmonic frequencies will be calculated too high for the intermolecular vibrations, and too low for the two NO stretch modes. Note as well that the

TABLE IV. Harmonic potential constants^a of (NO)₂.

Parameter	Fit 2, Ref. 9	Fit 3	Present <i>ab initio</i>
f_r	14.684(14)	14.662(34)	14.410
f_R	0.308(69)	0.195(15)	0.358
f_α	0.782(61)	0.671(17)	1.004
f_τ	0.036(9)	0.0342(24)	0.096
$f_{r\alpha}$			0.215
$f_{R\alpha}$	0.269(47)	0.155(16)	0.233
$f_{\alpha\alpha}$		-0.100(16)	-0.231
f_{rr}	0.783(12)	0.759(34)	0.855
f_{Rr}	0.637(150)	0.274(92)	0.050
$f_{R\alpha'}$			-0.394

^aUnits correspond to energies in aJ, bond lengths in Å, and angles in radians.

neglect of anharmonicity causes each harmonic frequency to be higher than the true fundamental frequency. Hence, the overestimation of the observed intermolecular fundamental frequencies (by 40–107 cm⁻¹, or 17%–63%) is disappointing but not altogether surprising. The ν_1 and ν_5 frequencies are underestimated by 0.3% and 3.0%, respectively.

These CCSD(T) vibrational frequencies are now the best available *ab initio* predictions for (NO)₂ by far, being considerably closer to the observed values than previous density functional theory predictions.²⁸⁻³⁰ Further improved *ab initio* predictions would only be achieved with more expensive methods which explicitly incorporate two reference electronic configurations, since it has been observed^{25,31} that the $(\sigma_{\text{NN}})^2 \rightarrow (\sigma_{\text{NN}}^*)^2$ configuration contributes strongly to the ground state wave function. Furthermore, since this second configuration has increased N–N antibonding character, its full inclusion would likely result in a more weakly bound dimer.

V. FORCE FIELD CALCULATIONS

We also made empirical harmonic potential calculations, as an extension of those described in Ref. 9. The observed data that are fitted are the vibrational frequencies and their isotopic variations, the centrifugal distortion constants, and the inertial defects. Ideally, these parameters should be corrected for anharmonicity, but this is not presently possible. Our previous force field (Fit 2) (Ref. 9) from 1995, calculated without knowledge of the intermolecular frequencies, agrees well with the new experimental values reported here (see Table III). The degree of agreement is probably fortu-

TABLE III. Observed and calculated intermolecular vibrational frequencies and isotope shifts of (NO)₂ (in cm⁻¹).

Vibration	Present Observed	Fit 2 force field, Ref. 9	Fit 3 force field	Fit 3 fractional ¹⁵ N shift ^a	Present <i>ab initio</i>
$\nu_2(a_1)$	239.361	259	242	-1.04%	279
$\nu_3(a_1)$	134.503	127	139	-2.37%	201
$\nu_4(a_2)$	117	119	117	-1.99%	191
$\nu_6(b_2)$	429.140	430	427	-1.88%	536

^aThis is the calculated Fit 3 fractional shift of the (¹⁵N¹⁶O)₂ frequency relative to (¹⁴N¹⁶O)₂.

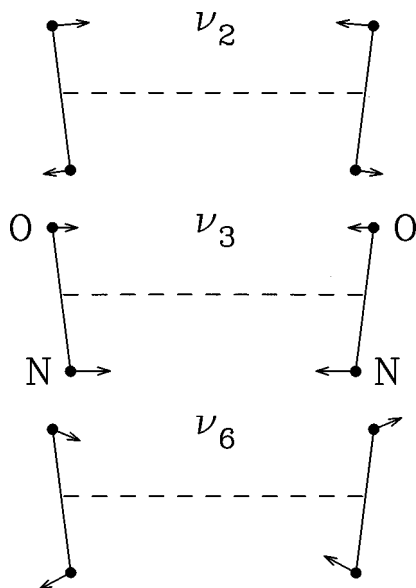


FIG. 6. Calculated normal mode motions for the ν_2 , ν_3 , and ν_6 vibrations of the NO dimer from the force field of Fit 3.

itous, but it does illustrate the value of accurate centrifugal distortion data in determining force fields. A repeat of Fit 2 (with $f_{r\alpha} = f_{\alpha\alpha} = f_{r\alpha'} = 0$) including the new data (except for ν_4) gave potential constants that agreed with the previous ones within their standard deviations; weighting of the data was similar to Ref. 9. When this fit was repeated with each of these three constants in turn also adjusted, the only significant improvement was for $f_{\alpha\alpha}$, which improved the fit by about 40% and gave $\nu_4 = 116 \text{ cm}^{-1}$. On the other hand, fits with $f_{\alpha\alpha}$ and either $f_{r\alpha}$ or $f_{r\alpha'}$ adjusted tended to jump to a solution with ν_4 greater than ν_3 , e.g., $\nu_4 = 158 \text{ cm}^{-1}$.

These results suggested a search for the allowed $\nu_5 \leftarrow \nu_4$ type-*c* band in the regions either 120 or 160 cm^{-1} below ν_5 . (Intermediate values near 135 cm^{-1} are unlikely because the large perturbing effect on the inertial defect of ν_3 would have been detectable in our analysis of ν_3 .) In general, type-*c* bands have a strong sharp feature near the band center. The candidate we have chosen is the feature at 1672 cm^{-1} (see Fig. 2), some 117 cm^{-1} below ν_5 , which is the strongest unassigned feature between 90 and 200 cm^{-1} below ν_5 . When this is included in the fits, the tendency to jump to a second solution is constrained. Variation of all three constants then gave a good fit, but their uncertainties were rather large. For the moment, we decided somewhat arbitrarily to constrain both $f_{r\alpha}$ and $f_{r\alpha'}$ to zero, giving the frequencies and potential constants shown as Fit 3 in Tables III and IV.

The nature of the normal mode motions is specified by the force fields, and there is general agreement between our *ab initio* and empirical results, although the exact distribution of motions between ν_2 and ν_3 is quite sensitive to the force field. The empirical (Fit 3) normal mode motions for ν_2 , ν_3 , and ν_6 are illustrated in Fig. 6 (note that ν_4 , the out-of-plane vibration, is completely determined by symmetry). The ν_2 vibration can be described as an antisymmetric combination of oscillating O–O and N–N distances, or, in

other words, as the symmetric in-plane bend. The ν_3 motion clearly corresponds to the dissociative intermolecular stretching mode, but neither ν_2 nor ν_3 correspond to a pure N–N stretch motion. And ν_6 is the antisymmetric bend. The predicted fractional ^{15}N isotope shifts from the Fit 3 force field are listed in Table III.

VI. CONCLUSIONS

In conclusion, the far-infrared spectrum of the gas phase NO dimer has been studied for the first time, and the locations of the four intermolecular modes have been determined. The values proposed here for these vibrational frequencies are rather different from previously accepted values, which were based on condensed phase experiments. In particular, the ν_6 mode is found to lie at a relatively high frequency (429 cm^{-1}) in rough accord with calculations, but not with previous experiments. The lack of agreement between the gas and condensed phase results in the present case is perhaps not surprising, both in view of the weak binding in $(\text{NO})_2$, which makes it especially susceptible to environmental perturbations, and in view of the sometimes considerable scatter in values among the various condensed phase experiments. In this context, it would be interesting to perform far infrared and Raman spectroscopy of the NO dimer in a neon matrix.

Our CCSD(T) *ab initio* calculation of the intermolecular frequencies agrees well with experiment in terms of their relative ordering, but consistently overestimates their values, due both to the neglect of anharmonicity and to an overestimation of the strength and rigidity of the intermolecular bonding in $(\text{NO})_2$. The multiconfigurational nature of the ground electronic state of the NO dimer makes accurate *ab initio* calculations of its properties a very challenging problem. No experimental evidence was seen in our spectra for other isomers of $(\text{NO})_2$, nor are any other stable isomers predicted by the CCSD(T) calculations.

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