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Nonpolar nitrous oxide dimer: Observation of combination bands of ($^{14}\text{N}_2\text{O}$) $_2$ and ($^{15}\text{N}_2\text{O}$) $_2$ involving the torsion and antigeared bending modes

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Spectra of the nonpolar nitrous oxide dimer in the region of the N_2O ν_1 fundamental band were observed in a supersonic slit-jet apparatus. The expansion gas was probed using radiation from a quantum cascade or a tunable diode laser, with both lasers employed in a rapid-scan signal averaging mode. Four bands were observed and analyzed: new combination bands involving the intermolecular conrotation of the monomers (A_g antigeared bend) for ($^{14}\text{N}_2\text{O}$) $_2$ and ($^{15}\text{N}_2\text{O}$) $_2$, the previously reported torsional combination band for ($^{14}\text{N}_2\text{O}$) $_2$ with improved signal-to-noise ratio, and the same torsional combination band for ($^{15}\text{N}_2\text{O}$) $_2$. The resulting frequencies for the intermolecular antigeared mode are 96.0926(1) and 95.4912(1) cm^{-1} for ($^{14}\text{N}_2\text{O}$) $_2$ and ($^{15}\text{N}_2\text{O}$) $_2$, respectively. This is the third of the four intermolecular frequencies which has now been measured experimentally, the others being the out-of-plane torsion and the geared bend modes. Our experimental results are in good agreement with two recent high level *ab initio* theoretical calculations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3697869>]

I. INTRODUCTION

The nitrous oxide dimer was one of the first weakly bound van der Waals complexes to be detected by means of infrared techniques in a supersonic jet expansion source. To date, two isomers of the dimer are known from experimental observations. The most stable isomer, which was detected first, has a planar nonpolar centrosymmetric (C_{2h}) geometry. It was first observed in the region of the $\nu_1 + \nu_3$ combination band of the monomer¹ and subsequently in the N_2O ν_3 ($\sim 1280 \text{ cm}^{-1}$) (Ref. 2) and ν_1 ($\sim 2220 \text{ cm}^{-1}$) (Ref. 3) regions. The second isomer of the dimer, observed only recently,^{4,5} is also planar but is polar with C_s symmetry. Since its discovery, there has been renewed interest in nitrous oxide dimer and as a result a number of experimental and theoretical studies have appeared in the literature. Experimental studies concerning the nonpolar isomer include the fully and partially substituted ^{15}N isotopologue,⁶ correction of an earlier assignment of the torsional combination band,⁷ and measurement of frequencies for the intermolecular torsional and geared bending modes⁸ with the help of theoretical *ab initio* results.⁹

On the theoretical side, two independent investigations of the spectrum of the nitrous oxide dimer have been carried out recently by constructing four-dimensional (rigid monomers) intermolecular potential energy surfaces at the CCSD(T) level.^{10–12} In both studies, the global minimum was found to be the nonpolar structure, with binding energies determined as -633 cm^{-1} by Dawes *et al.*¹⁰ and -628 cm^{-1} by Zheng *et al.*¹² Both studies found the polar isomer to be the second

most stable form, with a binding energy of -465 cm^{-1} . Low lying vibrational levels were also computed. Of particular interest to the present work are frequencies for the intermolecular vibrational modes which are listed in Table I. We successfully used these results to search for the combination band involving the in-plane antigeared mode around 2325 cm^{-1} and observed the expected band.

In the present paper, we report the observation of four bands of the nonpolar nitrous oxide dimer in the N_2O ν_1 region. First, the previously observed⁷ torsional combination band of ($^{14}\text{N}_2\text{O}$) $_2$ was re-measured as part of our initial setup of a new quantum cascade laser (QCL) source in our apparatus. We then took advantage of this laser's wide tuning range to observe the analogous torsional band of ($^{15}\text{N}_2\text{O}$) $_2$. A new combination band involving the intermolecular antigeared vibration was observed for ($^{14}\text{N}_2\text{O}$) $_2$ using one of our older tunable diode laser (TDL) sources, and for ($^{15}\text{N}_2\text{O}$) $_2$ using the QCL. The frequency for the intermolecular antigeared mode was determined to be 96.0926(1) cm^{-1} for ($^{14}\text{N}_2\text{O}$) $_2$, in excellent agreement with the calculated values of 97.5221 (Ref. 10) and 97.171 cm^{-1} .¹²

The observations reported here demonstrate the successful application of a continuous wave external cavity QCL in our apparatus while retaining the advantages of the rapid-scan signal averaging technique. They also represent the determination of another intermolecular frequency for the N_2O dimer, adding the antigeared bend to the previously observed out-of-plane torsion⁷ and in-plane geared bend modes.⁷ These intermolecular vibrations provide clear spectroscopic data against which theory can be benchmarked. The last remaining intermolecular frequency, which has not been measured is the van der Waals stretch.

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TABLE I. Intermolecular vibrational frequencies for the nonpolar ($^{14}\text{N}_2\text{O}$)₂ (in cm^{-1}).

Intermolecular mode	CCSD(T)F12b/VTZ-F12 ^a	CCSD(T) Aug-cc-pVDZ ^b	Experiment
Out-of-plane torsion (A_u)	25.8	26.5	27.3 ^{c,e}
In-plane geared (B_u)	41.9	39.5	42.3(1.0) ^d
Dissociation (A_g)	52.8	51.5	
In-plane antigeared (A_g)	97.5	97.2	96.0926(1) ^e

^aReference 10.^bReference 12.^cReferences 7 and 9.^dReferences 8 and 9.^eThis work.

II. EXPERIMENTAL DETAILS

Spectra were recorded at the University of Calgary using a previously described pulsed supersonic jet apparatus.⁴⁻⁷ The expansion gas was a mixture of 0.3% $^{14}\text{N}_2\text{O}$ or $^{15}\text{N}_2\text{O}$ in helium with a backing pressure of 7.5 atm. The isotopically enriched sample of $^{15}\text{N}^{15}\text{N}^{16}\text{O}$ was obtained from Icon Isotopes and had a stated atomic purity of 99%. Three of the bands reported here were measured using the QCL, and one which lies around 2325 cm^{-1} , outside its tuning range, was recorded with a Pb-salt TDL.

Chemical physics applications of quantum cascade lasers have recently been reviewed.¹³ Our QCL was a continuous wave device manufactured by Daylight Solutions Inc., operating between about 2140 and 2265 cm^{-1} . Since wavelength modulation speed was limited by its external cavity nature, it was not clear initially whether we could apply our usual rapid-scan signal averaging data acquisition technique with the QCL. Fortunately, however, this did prove possible, although it was necessary to reduce the repetition rate to 625 Hz from the usual 1 kHz used with TDL sources. Experimental details of the wavelength and temperature stabilization of the QCL and implementation of the data acquisition will be detailed in a future publication. The length of the jet opening was 2.5 ms and the spectra were averaged between 1800 to 2500 jet pulses for the TDL and 300 to 700 pulses for the QCL. Simultaneous etalon (free spectral range of 0.00997 cm^{-1}) and $^{14}\text{N}_2\text{O}$ reference gas spectra were recorded to perform frequency interpolation and absolute calibration, respectively.

III. RESULTS AND ANALYSIS

A. Antigeared combination band for ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂

The point group symmetry of the vibrationally averaged structure of the nonpolar nitrous oxide dimer is C_{2h} . This means that the two N_2O monomers forming the dimer are indistinguishable (if they are the same isotopologue) and there are two intramolecular vibrations in the ν_1 monomer stretch region: an in-phase vibration of the two monomers (with A_g symmetry) which is infrared inactive and an out-of-phase vibration (with B_u symmetry) which gives rise to the observed dimer fundamental band at 2229.4826 cm^{-1} .⁷ The dimer has four low frequency intermolecular van der Waals modes: out-of-plane torsion (A_u symmetry), in-plane geared bend (B_u), in-plane antigeared bend (A_g), and dissociation (or van der Waals stretch, A_g).

There are four infrared active binary combination bands in the monomer ν_1 region. Two of these have been observed previously, at 2249.360 and 2264.373 cm^{-1} .⁷ The first is the torsional combination band whose upper state is the sum of the A_g intramolecular vibration together with the A_u intermolecular torsion, giving rise to a c-type band. The second is the in-plane geared bend, whose upper state is the sum of the A_g intramolecular vibration together with the B_u intermolecular geared bend. One therefore expects, and observes,⁷ a hybrid band with a- and b-type rotational transitions. The upper states for the other two allowed combination bands also have B_u symmetry as they arise from the B_u intramolecular stretch with the A_g antigeared bend or the A_g van der Waals stretch.

According to the discussion in the previous paragraph, the combination band involving the antigeared mode should occur around 2325 cm^{-1} , since it is the sum of the out-of-phase infrared active intramolecular vibration, at 2229.483 cm^{-1} and the antigeared frequency, 97.5 cm^{-1} as calculated by Dawes *et al.*¹⁰ Here, we assume that the effect of the monomer vibrations on the intermolecular forces is small, so that the intermolecular vibrational frequencies are very similar in the ground and excited intramolecular states.

Using a TDL we searched a 5 cm^{-1} window around 2325 cm^{-1} and found this band. It was centered at 2325.575 cm^{-1} and had the expected hybrid (a- and b-type) rotational structure. A portion of the spectrum is shown in the top trace of Fig. 1. The rotational assignment and fitting of the band was successfully made by fixing the lower state parameters to those for the ground state of nonpolar ($^{14}\text{N}_2\text{O}$)₂, thus confirming that it was indeed a combination involving a low frequency intermolecular vibration. The corresponding band for ($^{15}\text{N}_2\text{O}$)₂ was easily located with a very similar separation between the combination band and the ν_1 fundamental. It was centered at 2255.659 cm^{-1} and its similarity to the combination band for ($^{14}\text{N}_2\text{O}$)₂ is clear in Fig. 1, provided allowance is made for the fact that the QCL spectrum has a somewhat larger line width due to laser drift during the data acquisition. Gaps in the experimental trace correspond to regions of strong N_2O monomer absorption. The second and fourth traces in Fig. 1 are simulated spectra, based on our rotational analyses, discussed below.

B. Torsional combination bands of nonpolar ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂

The torsional combination band of nonpolar ($^{14}\text{N}_2\text{O}$)₂ was selected as our test case for implementation of the QCL

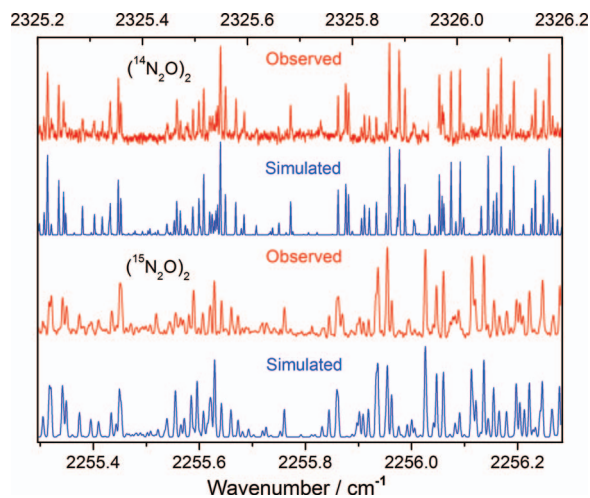


FIG. 1. Observed and simulated spectra of the nonpolar ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ dimer in the region of the N_2O ν_1 fundamental showing the antigeared combination bands. Rotational temperature for the simulated spectra was 2.5 K, and line widths were 0.0018 cm^{-1} for ($^{14}\text{N}_2\text{O}$)₂ which was recorded with a TDL and 0.003 cm^{-1} for ($^{15}\text{N}_2\text{O}$)₂ which was recorded with a QCL. Blank regions in the observed traces correspond to regions of strong N_2O monomer absorption. The upper wavenumber scale refers to the top two traces, and the lower scale to the bottom two traces.

source with rapid-scan signal averaging and continuous background subtraction for the following reasons: (1) it occurs around 2249 cm^{-1} ,⁷ which is within the range of the QCL; (2) it provides a critical sensitivity test because it is 500 to 1000 times weaker than the ν_1 fundamental of the dimer;¹¹ and (3) because of its weakness, it tests the stability of the QCL over many jet pulses (averaging times of 10 min or more). As was mentioned earlier, this combination band has a c-type rotational structure and a portion of the spectrum obtained with the QCL is shown in the top trace of Fig. 2. The quality of the spectrum is clearly excellent; even the very weak lines in the simulated spectrum (second trace in Fig. 2) are faithfully reproduced. This spectrum is greatly superior to those originally reported in Fig. 1 of Ref. 7.

The corresponding band for ($^{15}\text{N}_2\text{O}$)₂ was easily located with a very similar separation relative to the ν_1 fundamental. It was centered at 2179.805 cm^{-1} . The central portion of the band is illustrated in the third trace of Fig. 2, and the fourth trace represents the simulated spectrum based on our analysis discussed in Sec. III C.

C. Analysis

We used the PGopher computer program¹⁴ for assignment and simulation of the spectra. The line assignments were simple due to the fact that we already had good ground state parameters which were held fixed in all subsequent fits.⁶

A total of 92 lines were assigned for the antigeared combination band of ($^{14}\text{N}_2\text{O}$)₂, with maximum values for J and K_a of 11 and 4, respectively. A good fit with an rms deviation of 0.0003 cm^{-1} was obtained by varying eight parameters, which are listed in the first column in Table II. The observed line positions and rotational assignments are given in Table A1 of supplementary material.¹⁵ As can be seen from

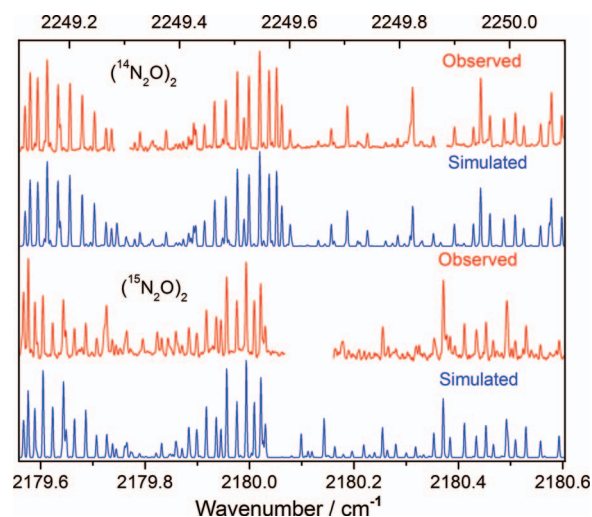


FIG. 2. Observed and simulated spectra of the ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ in the region of the ν_1 fundamental vibration of N_2O showing the torsional combination bands. Rotational temperature for the simulated spectra is 2.5 K, and line widths were 0.0018 cm^{-1} . Blank regions in the observed traces correspond to regions of strong N_2O monomer absorption. The upper wavenumber scale refers to the top two traces, and the lower scale to the bottom two traces.

the top two traces in Fig. 1, the match between the experimental and simulated spectra, which used the parameters listed in Table II, is excellent. For the simulated spectra we used a rotational temperature of 2.5 K, line width of 0.0018 cm^{-1} , and a relative transition moments of a-type/b-type = $\sqrt{1.5}$.

We assigned and fitted only 49 transitions for the combination band of ($^{15}\text{N}_2\text{O}$)₂, because many lines with higher values of J and K_a lines were found to be perturbed. However, a reasonable fit with an rms deviation of 0.0004 cm^{-1} was obtained by varying eight parameters in the upper state. The values obtained are listed in the third column of Table II. The observed line positions and rotational assignments for this band are given in Table A2 of supplementary material.¹⁵ The third and fourth traces in Fig. 1 show portions of the experimental and associated simulated spectra and as can be seen the match between them is not as good as that for ($^{14}\text{N}_2\text{O}$)₂. The

TABLE II. Molecular parameters for the antigeared combination bands of nonpolar ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ (in cm^{-1}).^a

	Nonpolar ($^{14}\text{N}_2\text{O}$) ₂		Nonpolar ($^{15}\text{N}_2\text{O}$) ₂	
	Upper state	Lower state ^b	Upper state	Lower state ^c
ν_0	2325.57517(7)		2255.6589(1)	
A	0.293378(36)	0.299409	0.28736(11)	0.294027
B	0.058749(6)	0.059925	0.055095(16)	0.056413
C	0.048743(5)	0.049836	0.046176(10)	0.047247
$10^5 \times \Delta_K$	1.21(24)	0.797	10.31(47)	0.581
$10^6 \times \Delta_{JK}$	1.62(99)	-1.23	10.07(22)	-1.23
$10^6 \times \Delta_J$	0.233(30)	0.158	0.449(88)	0.160
$10^7 \times \delta_J$	0.47(27)	0.46	1.84(99)	0.24

^aQuantities in parentheses correspond to 1σ from the least-squares fit, in units of the last quoted digit.

^bGround state parameters for nonpolar ($^{14}\text{N}_2\text{O}$)₂ (Ref. 6).

^cGround state parameters for nonpolar ($^{15}\text{N}_2\text{O}$)₂ (Ref. 6).

TABLE III. Molecular parameters for the torsional combination bands of the nonpolar ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ (in cm^{-1}).^a

	Nonpolar ($^{14}\text{N}_2\text{O}$) ₂		Nonpolar ($^{15}\text{N}_2\text{O}$) ₂	
	Upper state	Lower state ^b	Upper state	Lower state ^c
ν_0	2249.35915(4)		2179.8054(1)	
A	0.2864012(98)	0.299409	0.281221(27)	0.294027
B	0.0594845(28)	0.059925	0.056062(11)	0.056413
C	0.0500802(25)	0.049836	0.047460(7)	0.047247
$10^5 \times \Delta_K$	-0.290(31)	0.797	0.581 ^d	0.581
$10^6 \times \Delta_{JK}$	-0.75(12)	-1.23	-1.23 ^d	-1.23
$10^6 \times \Delta_J$	0.201(10)	0.158	0.163(55)	0.160
$10^7 \times \delta_J$	0.684(93)	0.46	1.11(46)	0.24

^aQuantities in parentheses correspond to 1σ from the least-squares fit, in units of the last quoted digit.

^bGround state parameters for nonpolar ($^{14}\text{N}_2\text{O}$)₂ (Ref. 6).

^cGround state parameters for nonpolar ($^{15}\text{N}_2\text{O}$)₂ (Ref. 6).

^dThis parameter was kept fixed at its ground state value.

agreement is even poorer at the high and low frequency sides of the band (not shown here).

The analysis of torsional combination bands proceeded in much the same way as for the antigeared combinations. One hundred thirty-two lines for ($^{14}\text{N}_2\text{O}$)₂ and 66 lines for ($^{15}\text{N}_2\text{O}$)₂ were assigned and fitted. The rms deviation of the fit for ($^{14}\text{N}_2\text{O}$)₂ was 0.0002 cm^{-1} and that for ($^{15}\text{N}_2\text{O}$)₂ was 0.00036 cm^{-1} . The larger deviation for ($^{15}\text{N}_2\text{O}$)₂ reflects a shorter averaging time and coverage of a smaller frequency window for the ($^{15}\text{N}_2\text{O}$)₂ spectrum to conserve the $^{15}\text{N}_2\text{O}$ sample. The parameters obtained are listed in the first and third columns of Table III for ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂, respectively. The observed line positions and rotational assignments for these bands are given in Table A3 and Table A4.¹⁵

IV. DISCUSSION AND CONCLUSIONS

As discussed in Sec. III A, the determination of the vibrational antigeared frequency from the combination band relies on the frequency of the out-of-phase vibration of the two monomers, which is experimentally known. This is $2229.4826(1) \text{ cm}^{-1}$ for ($^{14}\text{N}_2\text{O}$)₂.⁷ The band center for the antigeared combination determined here is $2325.57517(7) \text{ cm}^{-1}$ (Table II), and we therefore obtain an antigeared vibrational frequency of $96.0926(1) \text{ cm}^{-1}$ for ($^{14}\text{N}_2\text{O}$)₂ in the excited N_2O ν_1 state. This is in very good agreement with the calculated values of 97.5 cm^{-1} from Dawes *et al.*¹⁰ and 97.2 cm^{-1} from Zheng *et al.*¹² Of course the calculations are for the ground vibrational state while the experimental value is for the excited N_2O ν_1 state, but in a sense the good agreement supports the idea that intramolecular vibrations do not significantly affect the frequency of this intermolecular mode. Similarly, the antigeared vibrational frequency for ($^{15}\text{N}_2\text{O}$)₂ is $2255.6589(1) - 2160.1676(1) = 95.4913(2) \text{ cm}^{-1}$.

The determination of the out-of-plane torsional frequency from the torsional combination band, on the other hand, relies on the frequency of the in-phase vibration of the two monomers, which is not experimentally known. In Ref. 7, we obtained estimates of -1.7 and -1.8 cm^{-1} for

TABLE IV. Observed intermolecular vibration frequencies for nonpolar ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ (in cm^{-1}).

Intermolecular mode	($^{14}\text{N}_2\text{O}$) ₂	($^{15}\text{N}_2\text{O}$) ₂
Out-of-plane torsion (A_u)	27.3(1.0)	26.9(1.0)
In-plane antigeared (A_g)	96.0926(1)	95.4913(1)

the vibrational shifts in ($^{14}\text{N}_2\text{O}$)₂ and ($^{15}\text{N}_2\text{O}$)₂ relative to the monomer band center. Using these vibrational shifts, we obtain torsional frequencies of $27.3(1.0) \text{ cm}^{-1}$ for ($^{14}\text{N}_2\text{O}$)₂ and $26.9(1.0) \text{ cm}^{-1}$ for ($^{15}\text{N}_2\text{O}$)₂, in the excited N_2O ν_1 state. The large error of 1.0 cm^{-1} in the torsional frequencies is indicative of the uncertainty in the true value of the infrared forbidden in-phase intramolecular frequency.^{8,9} Table I gives a comparison between the experimental and theoretical values for the intermolecular frequencies of the nonpolar nitrous oxide dimer and Table IV lists the intermolecular frequencies determined in this work.

Comparing the changes in rotational parameters between ground and excited states, we observe that there is a relatively large decrease in A for the antigeared combination state, $\Delta A = -180 \text{ MHz}$. Such large changes in A are usually attributed to a-type Coriolis interactions of the type $-2(A\zeta)q_{anti}p_iJ_a$, where q_{anti} and p_i are the normal coordinates for the antigeared mode and momentum conjugate to the normal coordinate q_i for the perturbing state, respectively. Since J_a and q_{anti} both have A_1 symmetry, the perturbing state must also have A_1 symmetry, i.e., $\Gamma(p_i) = A_1$. The associated correction to A is then given by $\Delta A = \sum_i \frac{4(A\zeta_i)^2}{(\omega_{anti} - \omega_i)}$. Here ω_{anti} is the antigeared frequency and ω_i is the frequency of the perturbing state. Possible perturbing states are the van der Waals stretch state ($\nu_r = 1$), at $\omega_1 = 52.8 \text{ cm}^{-1}$, the state with four torsional quanta excited ($\nu_t = 4$), at 98.2 cm^{-1} , and the van der Waals stretch state with $\nu_r = 2$, at $\omega_2 = 101.9 \text{ cm}^{-1}$, as listed in Table VI of Dawes *et al.*¹⁰ Dawes *et al.* also report two-dimensional probability density plots for intermolecular modes and indicate that the coupling between the torsional states up to $\nu_t = 7$ and other coordinates is weak. If we exclude $\nu_t = 4$ from the list of possible perturbing states, we are then left with two contributions:

$$\Delta A_1 = \frac{4(A\zeta_1)^2}{(\omega_{anti} - \omega_1)} = \frac{0.359\zeta_1^2}{44.75} = .0080\zeta_1^2 \geq 0$$

and

$$\Delta A_2 = \frac{4(A\zeta_2)^2}{(\omega_{anti} - \omega_2)} = \frac{0.359\zeta_2^2}{-4.39} = -0.0818\zeta_2^2 \leq 0.$$

If $\zeta_1 \leq 0.3$, this means that $\Delta A = \Delta A_2$ and $\zeta_2 \approx 0.27$. If, on the other hand, $\zeta_1 \approx 1$ then $\Delta A = \Delta A_1 + \Delta A_2 = +0.008 + \Delta A_2$ which results in a larger coupling constant ($\zeta_2 \approx 0.41$) between $\nu_r = 2$ and the antigeared mode. It should be noted that the value of ζ_2 is subject to a considerable uncertainty because the calculated value of $(\omega_{anti} - \omega_2)$ is very small. Whatever the case may be, we conclude that the antigeared mode couples rather strongly to the van der Waals stretching

mode, in accord with the two-dimensional probability density plots of Dawes *et al.*

We have now observed combination bands involving three out of the four intermolecular modes of nonpolar N₂O dimer. What about the remaining one, the van der Waals stretching mode? According to theory,^{10,12} this combination band occurs around 2282 cm⁻¹ for (¹⁴N₂O)₂, outside the frequency range of the QCL, and we are also unable to access this window with our TDLs. However, the analogous band for (¹⁵N₂O)₂ which occurs around 2212 cm⁻¹ can be accessed by the QCL. Our attempts to observe this combination band have not been successful, suggesting that it may be very weak, although we have detected its counterpart for the nonpolar OCS dimer with good signal-to-noise ratio.¹⁶

In summary, four infrared bands of the nonpolar nitrous oxide dimer in the N₂O ν₁ region were observed. A TDL was used to observe the antigeared combination of (¹⁴N₂O)₂ near 2325 cm⁻¹ and a cw QCL was employed to observe the antigeared and the torsional combination bands for (¹⁵N₂O)₂ as well as the torsional combination band for (¹⁴N₂O)₂. Both lasers were used in the rapid-scan signal averaging mode and the clusters were generated by a pulsed supersonic jet apparatus. The frequency for the intermolecular antigeared mode was determined to be 96.0926(1) cm⁻¹ for (¹⁴N₂O)₂ which is in very good agreement with theoretical calculations. This is the third of the four intermolecular frequencies which has now been measured experimentally, the others being the out-of-plane torsion and the geared bend modes. The last remaining intermolecular frequency, which has not been measured so far, is the van der Waals stretch.

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- ¹⁶Unpublished data.