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N₂O clusters in a supersonic jet studied by matrix-isolation infrared spectroscopy and density functional theory calculation

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Abstract

N₂O clusters in a supersonic jet were isolated in a low-temperature argon matrix. The infrared bands of the clusters were assigned with the aid of the results of density functional theory (DFT) calculation where the 6-31 + G* basis set is used to optimize geometrical structures. It is concluded that the N···O interacting antiparallel conformer is the most stable dimer. This result supports the high-resolution infrared spectroscopic study of Huang and Miller [J. Chem. Phys. 89 (1988) 5408], but disagrees with the recent matrix-isolation study of Nxumalo and Ford [J. Mol. Struct. 327 (1994) 145]. The observed dependence of cluster formation on stagnation pressure is used to examine the cooling effect on supersonic expansion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: N₂O clusters; Matrix isolation; Supersonic jet; Fourier transform infrared spectroscopy; Density functional theory calculation

1. Introduction

Numerous van der Waals clusters have been studied in the gas phase by using molecular beam techniques [1,2]. However, the relative populations of clusters formed by this technique are so small that highly sensitive laser systems are necessary to measure the spectra of these clusters. The populations can be increased by low-temperature matrix-isolation, which can accumulate clusters in solid argon [3], and conventional spectrophotometers can readily be used to measure infrared, Raman and UV–visible spectra. We combined this method with the molecular beam technique to study conformational cooling in a

supersonic jet of 1,2-dichloroethane and found that the ratio of the *trans* and *gauche* conformers in a supersonic jet is maintained in an argon matrix without redistribution [4]. In the present study, we have isolated N₂O clusters produced by a supersonic expansion through a pulsed nozzle in low-temperature argon matrices in order to study cluster formation. The observed infrared spectra of N₂O clusters are assigned with the aid of the density functional theory (DFT) calculation where the 6-31+G* basis set is used to optimize geometrical structures.

The N₂O dimer was previously studied by Ohshima et al. [5,6] and Miller et al. [7,8]. Both the groups used the molecular beam technique with high-resolution laser spectroscopy in the gas phase. Huang and Miller [8] analyzed the vibrational–rotational lines of the N₂O dimer and determined the rotational constants; they estimated the structure to be the N···O

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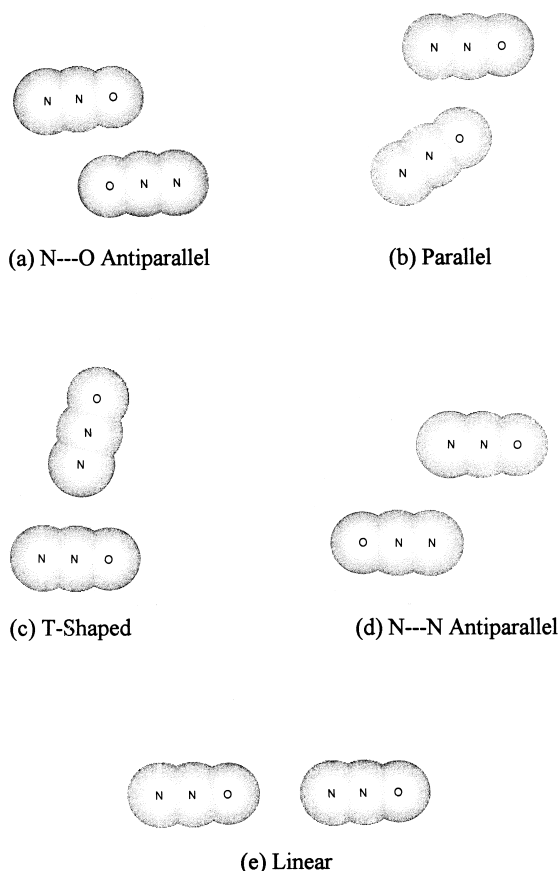


Fig. 1. Optimized geometry of N_2O dimers.

interacting antiparallel conformer, as shown in Fig. 1(a), where the nitrogen atom of one N_2O molecule interacts with the oxygen atom of the other. Nxumalo et al. studied the N_2O dimer by ab initio calculation

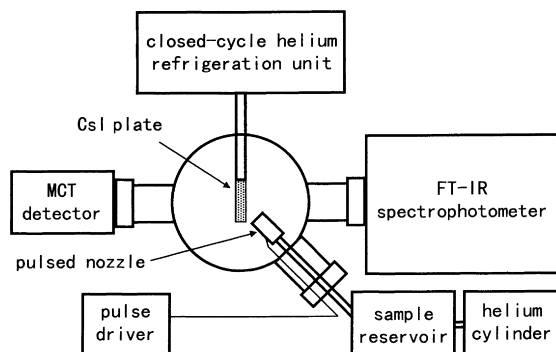


Fig. 2. Schematic figure of the experimental setup.

[9] and low-temperature matrix-isolation infrared spectroscopy using an effusive source [10]. The structure proposed by them is the $\text{N}\cdots\text{N}$ antiparallel conformer, as shown in Fig. 1(d), where two pairs of nitrogen atoms interact with each other. The structure of the N_2O dimer proposed by the matrix isolation method is totally different from that derived by the molecular beam technique. In order to solve this discrepancy, we have studied N_2O dimers by matrix-isolation infrared spectroscopy combined with the molecular beam technique and DFT calculation. In this paper, we also discuss cluster formation in a supersonic jet by measuring the spectral changes caused by changing stagnation pressures.

2. Experimental details

A combination system of matrix isolation and molecular beam technique was first proposed by Günthard et al. [11] and then developed by Knözinger et al. [12–14]. A schematic figure of our experimental system is shown in Fig. 2, where neither skimmer nor differential pumping system is used.

The N_2O sample (Showa Denko, 99.99% purity) was diluted with argon gas (Nippon Sanso, 99.9999% purity) in a glass cylinder. The premixed sample gas was transferred into a stainless steel reservoir and pressed by helium gas (Nippon Sanso, 99.999% purity). The mixing ratios of $\text{N}_2\text{O}/\text{Ar}/\text{He}$ were about 1/5000/5000, 1/5000/15 000 and 1/5000/25 000 at the stagnation pressure of 1, 2 and 3 atm, respectively. The sample gas was expanded through a pulsed nozzle (General Valve) and deposited directly in a vacuum chamber on a CsI plate, cooled by a closed cycle helium refrigeration (CTI Cryogenics, Model M-22) at about 15 K. The helium gas was quickly pumped out after collision at the cold plate, the temperature of which was monitored by a thermocouple. The distance from the nozzle to the cold CsI plate was 20 mm. The diameter of the nozzle was 300 μm . The pulse width and the pulse interval were fixed to 160 μs and 1.0 Hz, respectively. Infrared spectra of the matrix samples were measured with an Fourier transform infrared spectroscopy (FTIR) spectrophotometer (JEOL, Model JIR-7000). The spectral resolution was 0.5 cm^{-1} , and the number

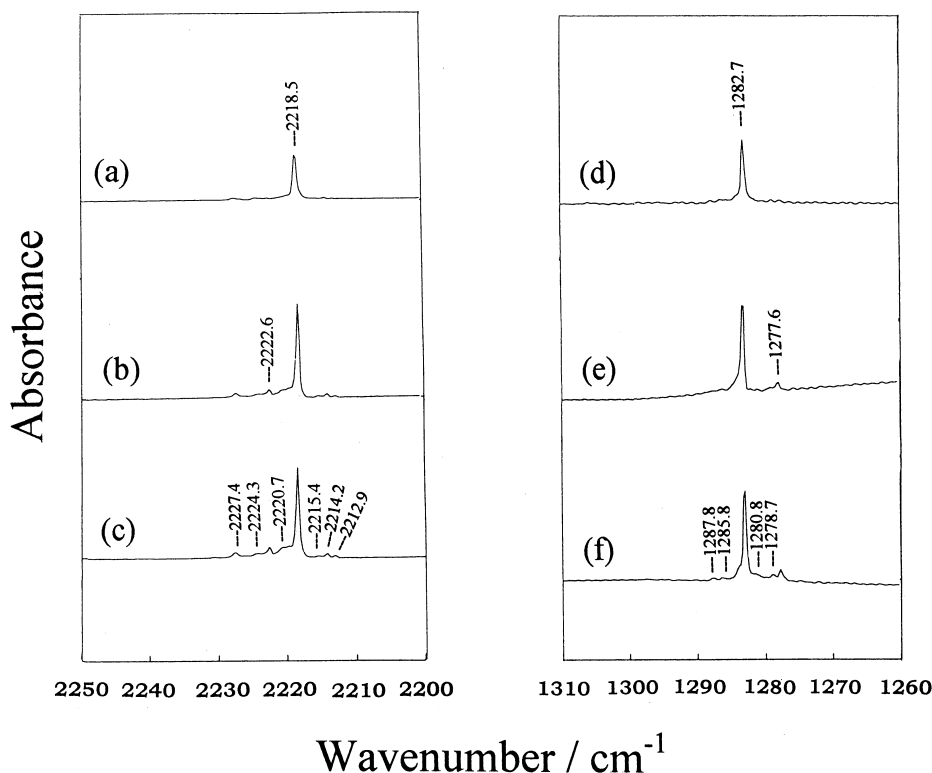


Fig. 3. Matrix-isolation infrared spectra of N_2O clusters generated by supersonic expansion. The stagnation pressures are: (a) and (d) 1 atm; (b) and (e) 2 atm; (c) and (f) 3 atm. $\text{N}=\text{O}$ stretching region is scaled so as to make the peak heights of the 1282.7 and 2218.5 cm^{-1} bands nearly equal.

of accumulation was 64. Other experimental details were reported elsewhere [4,15].

3. Results

3.1. Stagnation pressure dependence

Since N_2O molecules prefer aggregation even in low-temperature argon matrices, a low-concentration sample of $\text{N}_2\text{O}/\text{Ar}$, 1/5000, was used in experiments of supersonic expansion. When the pure $\text{N}_2\text{O}/\text{Ar}$ sample was directly deposited on a low-temperature CsI plate after supersonic expansion at the stagnation pressure of 1 atm, the observed spectra showed the bands of larger-size N_2O clusters produced by aggregation. Then the sample gas was pressed by helium gas in a reservoir to avoid the aggregation, and to keep the mixing ratio of 1/5000 in matrices. It was found by

monitoring the temperature of the CsI plate that heat load due to helium gas was negligible in the present study. Fig. 3(a) and (d) shows infrared spectra of the matrix sample when the total pressure of the mixing gas in the reservoir was 1 atm. Two strong bands were observed at 2218.5 and 1282.7 cm^{-1} in the $\text{N}\equiv\text{N}$ and $\text{N}=\text{O}$ stretching regions, respectively. They were easily assigned to N_2O monomer; their wavenumbers agreed with those reported by Sodeau and Withnall [16] within 0.2 cm^{-1} .

When the stagnation pressure of the same sample was elevated to 2 atm by addition of helium gas, several new peaks were clearly observed in the $\text{N}\equiv\text{N}$ and $\text{N}=\text{O}$ stretching regions, as shown in Fig. 3(b) and (e). The intensities of these peaks slightly increased when the stagnation pressure was elevated to 3 atm, as shown in Fig. 2(c) and (f). The temperature of a supersonic jet decreases with the stagnation pressure [4]. These small bands were

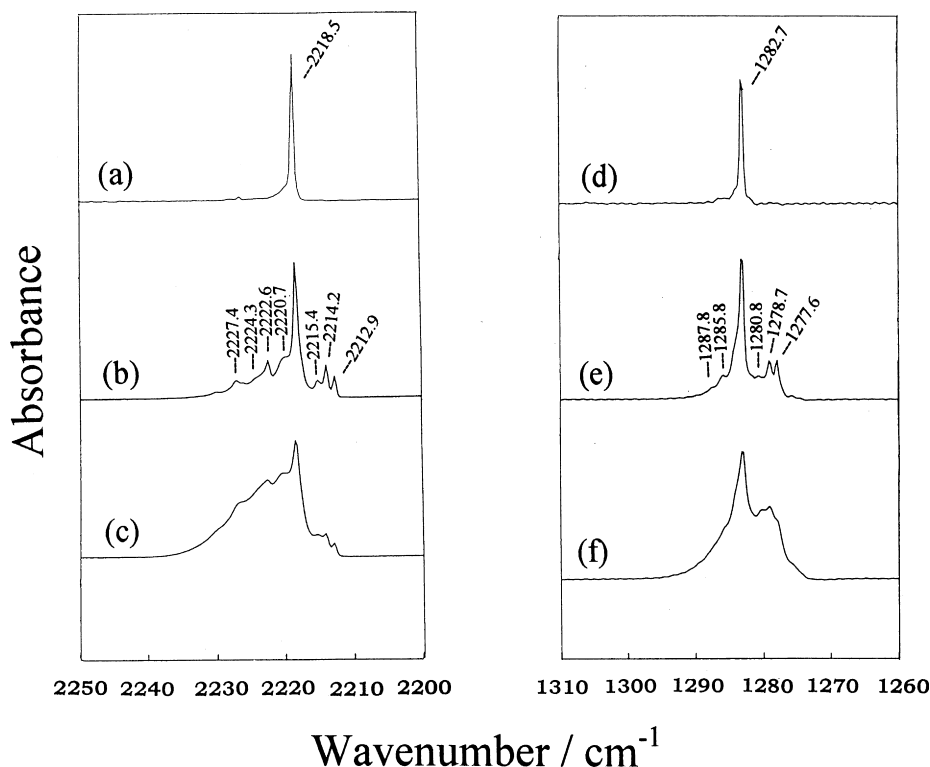


Fig. 4. Matrix-isolation infrared spectra of N_2O clusters deposited by effusive nozzle. The mixing ratio of $\text{N}_2\text{O}/\text{Ar}$ are (a) and (d) 1/5000; (b) and (e) 1/1000; (c) and (f) 1/200. The $\text{N}=\text{O}$ stretching region is scaled so as to make the peak heights of the 1282.7 and 2218.5 cm^{-1} bands nearly equal.

Table 1
Calculated energy differences of N_2O clusters from monomer (in kJ/mol)

	Conformer	B3LYP/6-31+G* (this work)	Previous studies
Dimer	$\text{N}\cdots\text{O}$ antiparallel	-2.920	-1.68 ^a
	Parallel	-1.857	-2.38 ^a
	T-shaped	-1.521	-2.80 ^a
	$\text{N}\cdots\text{N}$ antiparallel	-1.041	-2.15 ^a
	Linear	-0.568	
Trimer	Cyclic planar I	-6.315	-13.77 ^b
	Nonplanar	-5.974	-14.81 ^b
	Cyclic planar II	-3.855	-11.80 ^b
	Linear	-1.115	

^a Ref. [9]. MP2/6-31G* was used.

^b Ref. [21]. MP2/6-31+G(2d,2p) was used.

assigned to N₂O clusters generated by supersonic expansion.

3.2. Concentration dependence

The low-temperature rare-gas matrix-isolation method was originally developed to remove intermolecular interactions, but this method has also been useful to study intermolecular interactions and van der Waals clusters by varying concentrations of matrix samples. We have measured infrared spectra of N₂O clusters by using an effusive nozzle for comparison with the results of supersonic expansion. Fig. 4(a) and (d) shows the infrared spectra of a diluted sample, with a mixing ratio of 1/5000. As described above, the bands observed at 2218.5 and 1282.7 cm⁻¹ are due to monomer. When the concentration was increased to 1/1000, the small peaks observed in the jet spectra were also observed clearly in Fig. 4(b) and (e). At a still higher concentration, 1/200, many infrared bands were overlapped and their peak positions were smeared, as shown in Fig. 4(c) and (f). These spectra are essentially identical to the results reported previously [10,16].

3.3. DFT calculation

In order to assign the infrared bands, we made a recalculation of the energies and the vibrational wavenumbers of N₂O clusters by the DFT method by using the GAUSSIAN94 program [17] with the 6-31+G* basis set, where the hybrid density functional [18], in combination with the Lee, Yang and Parr correlation functional (B3LYP) [19], was used to optimize the geometrical structures. The calculated structures for five dimers are shown in Fig. 1 and the corresponding relative energies are given in Table 1. The N⋯O interacting antiparallel conformer is found to be the most stable. The energy of this conformer is lower than twice that of the monomer by 2.92 kJ/mol. The second stable dimer is the parallel conformer. Strictly speaking, two molecular axes of the N₂O molecules in this dimer are slightly inclined. The four nonlinear conformers are more stable than the linear conformer by more than 0.47 kJ/mol, probably because the quadrupole moment of N₂O molecule plays a more important role in cluster formation than on the dipole moment. The net charges on the terminal nitrogen and oxygen atoms are slightly negative, -0.2112

and -0.1763, whereas that on the central nitrogen atom is positive, +0.3875. This implies that the terminal nitrogen or oxygen atom of one N₂O molecule effectively interacts in cluster formation with the central nitrogen atom of the other N₂O molecule in all but the linear conformer.

4. Discussion

4.1. Geometry and energy of dimers

Huang and Miller [8] analyzed the vibrational-rotational spectra of the dimer generated by supersonic expansion and obtained the rotational constants of two isotopic species: (¹⁴N¹⁴N¹⁶O)₂ and (¹⁵N¹⁴N¹⁶O)₂. From these constants they concluded that the N₂O dimer prefers the N⋯O interacting antiparallel conformation (Fig. 1(a)). On the other hand, Nxumalo et al. reached a different conclusion from their analysis of infrared bands of clusters in low-temperature matrices. They compared the wavenumber shifts from the monomer bands with the values obtained by an MP2 calculation and concluded that the N⋯N interacting antiparallel conformer (Fig. 1(d)) was stable in low-temperature matrices though not in the lowest. The results reported by Nxumalo et al. are shown in Table 1, where the N⋯N antiparallel conformer is more stable than the N⋯O antiparallel conformer. On the contrary, our calculations have reached the conclusion that the N⋯O antiparallel conformer is the most stable, whereas the N⋯N antiparallel conformer is the least stable among the four nonlinear conformers. This finding supports the conclusion of Huang and Miller [8].

4.2. Conformational assignments of dimer

As shown in Fig. 3(b) and (e), the most intense dimer peaks observed at 2222.6 and 1277.6 cm⁻¹ in the N≡N and N=O stretching regions, respectively, shift from those of the monomer by +4.1 and -5.1 cm⁻¹. These bands are probably those observed by Nxumalo et al. [10]. They concluded that these bands were due to the N⋯N antiparallel conformer, judging from the calculated shifts for the N≡N and N=O stretching modes with a blue shift of +4 cm⁻¹ and a red shift of -1 cm⁻¹, respectively [9]. Our shifts calculated by the DFT method are opposite: for the

Table 2

Observed and calculated wavenumbers of N₂O clusters (in cm⁻¹)

Vibrational mode	Wavenumber	Shift		Tentative assignments
		Observed	Calculated	
N≡N stretching	2227.4	+8.9	+7.9	Nonplanar (trimer)?
	2224.3	+5.8	+7.7	Cyclic planar I (trimer)?
	2222.6	+4.1	+5.2	N···O antiparallel
	2220.7	+2.2	+2.5	T-shaped
	2219.7 ^a	+1.2	+1.7	Parallel
	2218.5	0	0	Monomer
	2215.4	-3.1	-1.1	N···N antiparallel
	2214.2	-4.3	-3.7	Linear dimer
	2212.9	-5.6	-5.6	Linear (trimer)?
N=O stretching	1287.8	+5.1	+3.5	T-shaped, parallel
	1285.8	+3.1	+2.5	N···N antiparallel
	1283.9 ^a	+1.2	+1.0	T-shaped
	1282.7	0	0	Monomer
	1280.8	-1.9	-1.7	Parallel
	1278.7	-4.0	-2.3	Linear dimer
	1277.6	-5.1	-3.6	N···O antiparallel

^a At shoulder of monomer bands.

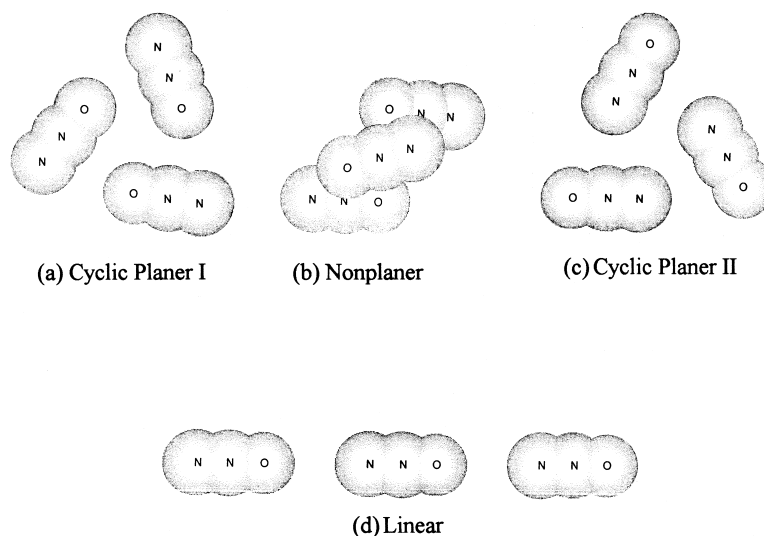
N···N antiparallel conformer the shifts are -1.1 and +2.5 cm⁻¹. On the other hand, the calculated shifts for the N···O antiparallel conformer are a blue shift of +5.2 cm⁻¹ and a red shift of -3.6 cm⁻¹ for the N≡N and N=O stretching modes, respectively. These values agree well with those observed in the matrix-isolation infrared spectra, +4.1 and -5.1 cm⁻¹. Therefore, we again support the assignment of Huang and Miller [8] that the N···O antiparallel conformer is the most stable N₂O dimer in a supersonic jet.

The energy differences among the conformers shown in Table 1 are so small that most of them are expected to be isolated in low-temperature argon matrices. The wavenumber shifts calculated by the DFT method are summarized and compared with the observed values in Table 2. As the T-shaped and parallel dimers have no center of symmetry, two vibrational modes are infrared active in each region. The shifts of N≡N stretching mode are +3.9 and +2.5 cm⁻¹ for the T-shaped conformer and +3.6 and +1.7 cm⁻¹ for the parallel conformer. Some of them are probably buried in the shoulder of the monomer bands. The shifts of N=O stretching mode are +3.5 and +1.0 cm⁻¹ for the T-shaped

conformer and +3.5 and -1.7 cm⁻¹ for the parallel conformers. They were observed at 1287.8, 1283.9 or 1280.8 cm⁻¹.

The 2214.2 cm⁻¹ band shows a shift of -4.3 cm⁻¹. This band cannot be assigned to any of the dimers except for the linear conformer; the corresponding N=O stretching mode for the linear conformer is expected to appear at 1278.7 cm⁻¹ with a shift of -4.0 cm⁻¹. These bands disappeared when the matrix sample was annealed at 28 K for 15 min. Thus we assign these bands to the linear conformer; the barrier height from the linear conformer to others is probably so small that the conformational change easily occurs by annealing.

Sodeau and Withnall [16] previously assigned the 2221.9, 2220.7, 2215.5, 2214.3 and 2213.1 cm⁻¹ bands in the N≡N stretching region and 1280.7, 1278.8 and 1277.7 cm⁻¹ bands in the N=O stretching region to dimers, but without conformational assignments. On the other hand, Gauthier [20] measured the FTIR bands of clusters generated in molecular beam, and assigned the 2228.0 and 1282.4 cm⁻¹ bands to a dimer. However, this assignment is doubtful because the concentration of the sample, 0.2%, was so high that larger clusters must have been produced.

Fig. 5. Optimized geometry of N_2O trimers.

4.3. Conformational assignments of trimer

The matrix-isolation infrared spectra of the sample cooled by supersonic expansion showed additional bands at 2227.4 and 2224.3 cm^{-1} . The wavenumber shifts from monomer are $+8.9$ and $+5.8\text{ cm}^{-1}$, respectively. As shown in Table 2, all the calculated shifts for dimers are between $+5.2$ and -3.7 cm^{-1} . Therefore, these bands cannot be assigned to any

Table 3
Calculated wavenumber shifts (in cm^{-1}) and relative intensities of trimers

Conformer	N \equiv N stretching		N=O stretching	
	Shift	Intensity	Shift	Intensity
Cyclic planar I	+7.7	0.55	+1.3	0.00
	+7.7	0.55	−0.9	0.11
	+6.5	0.00	−0.9	0.11
Nonplanar	+7.9	0.60	+1.5	0.05
	+4.9	0.32	−2.6	0.02
	+3.4	0.12	−4.6	0.15
Cyclic planar II	+6.9	0.00	+6.4	0.09
	+3.9	0.58	+6.4	0.09
	+3.9	0.58	+4.5	0.00
Linear	+1.5	0.05	0.0	0.03
	−0.8	0.00	−1.8	0.00
	−5.6	1.23	−3.0	0.19

dimers. Hence, we also made a DFT calculation for N_2O trimers to calculate their wavenumbers. The obtained optimized geometrical structures are shown in Fig. 5 and the relative energies are listed in Table 1. Our results are inconsistent with those reported by Miller and Pedersen [21], who used a larger basis set, 6-31+G(2d,2p), with the MP2 method. However, the level of our calculation seems to be sufficient to get reasonable estimates on wavenumbers, as shown in our previous studies on HCN clusters, where the calculated wavenumber shifts agree well with the corresponding experimental data [15]. The calculated shifts and relative intensities of N_2O trimers are summarized in Table 3. The cyclic planar I and nonplanar conformers show blue shifts of about 8 cm^{-1} for the N \equiv N stretching mode. Therefore, we tentatively assign the 2227.4 and 2224.3 cm^{-1} peaks to the trimers. The 2212.9 cm^{-1} band with a shift of -5.6 cm^{-1} is lower than that of the linear dimer. Hence, we tentatively assign this band to the linear trimer with a calculated shift of -5.6 cm^{-1} . The relative intensity of the linear trimer is predicted to be very high by the DFT calculation as shown in Table 3, although it is the least stable conformer among the trimers. No corresponding N=O stretching bands of the trimers were found in the spectra, probably because they were buried in the bands of dimers or the monomer.

4.4. Comparison of supersonic jet with effusive source

One must consider two factors for the production of N_2O clusters in the present experiments: the cooling effect of supersonic expansion and the concentration effect. Since N_2O molecules easily aggregate in low-temperature matrices, it is necessary to dilute the N_2O gas with argon 5000 times for observation of infrared bands due to monomer. However, it seems hard to observe the bands of only small-size clusters such as dimers or trimers by simply controlling the concentration. Then we tried to generate dimers by supersonic expansion of the efficiently diluted sample, where the cooling effect was so large that we could not assign the bands of dimers among many bands of the larger-size clusters. In order to get the most suitable condition to generate dimers, the sample gas was pressed by helium, because the cooling effect of helium is smaller than that of argon. When the stagnation pressure of the sample was 1 atm, the matrix-isolation spectra (Fig. 3(a) and (d)) were similar to those of the effusive source (Fig. 4(a) and (d)). This finding implies that the cooling effect of supersonic expansion is too small to produce N_2O clusters under this stagnation pressure. However, infrared bands of N_2O clusters were observed when the stagnation pressure of the same sample was increased to 2 atm. This means that clusters were generated in a supersonic jet and isolated in an argon matrix. The matrix-isolation infrared spectra of a supersonic jet expanded under 3 atm were not significantly different from those under 2 atm. This is not surprising because the cooling effect is mostly constant at pressures higher than 2 atm, as reported in the conformational cooling of 1,2-dichloroethane [4].

5. Conclusions

We have observed the infrared spectra of a supersonic jet of N_2O by depositing on a cold CsI plate. When the stagnation pressure of supersonic expansion was adjusted to 1 atm, only N_2O monomer bands were observed in the infrared spectra of low-temperature argon matrices. N_2O dimer bands were also observed when the pressure was increased to 2 atm. With the aid of the DFT calculation, they were assigned to the $\text{N}\cdots\text{O}$ antiparallel, parallel, T-shaped, $\text{N}\cdots\text{N}$ antiparallel and linear conformers, where the $\text{N}\cdots\text{O}$ antiparallel

conformer is the most stable. N_2O trimer bands with large shifts of +8.9, +5.8 or -5.6 cm^{-1} in the $\text{N}\equiv\text{N}$ stretching region were observed and tentatively assigned to the cyclic planar, nonplanar and linear conformers.

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