Buffer-gas pressure broadening for the $(0\ 0^0\ 3) \leftarrow (0\ 0^0\ 0)$ band of N_2O measured with continuous-wave cavity ring-down spectroscopy

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Abstract Buffer-gas pressure broadening for the $(0\ 0^0\ 3) \leftarrow (0\ 0^0\ 0)$ band of N_2O was investigated with continuous wave cavity ring-down spectroscopy within the temperature range of 243-353 K. The measured absorption profiles were analyzed with Voigt functions. The pressure broadening coefficients, $\gamma(\text{gas})$, and the temperature dependent parameters (broadening exponent) were determined for a variety of buffer gases: N_2 , O_2 , He, Ne, Ar, Kr, and Xe. $\gamma(\text{air})$ values were also determined using $\gamma(\text{N}_2)$ and $\gamma(\text{O}_2)$. The effective potential well depth for $(\text{N}_2\text{O})_2$ under room temperature was estimated from $\gamma(\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe})$ using the Permenter-Seaver's model, and the results were compared with theoretical calculations. Simultaneously, the effective potential well depth for $(\text{CO}_2)_2$ is discussed.

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1. Introduction

Nitrous Oxide (N_2O) is an important trace constituent of the Earth's atmosphere as one of the major greenhouse gases in the troposphere, with a global warming potential of 280 times greater than that of CO_2 . According to the IPCC report [1], the atmospheric burden of N_2O continues to increase by about $0.2\text{-}0.3\text{ }\% \text{yr}^{-1}$. In the stratosphere, N_2O is known as a main source of NO_x ($\text{NO} + \text{NO}_2$), which control the concentration of ozone through catalytic ozone destruction cycles [2]. Precise line parameters are needed for spectroscopic remote sensing, especially for global satellite and ground-based measurements of the concentration and distribution of molecules in the Earth's atmosphere. The line profile data in the infrared region have been accumulated with use of Fourier transform infrared and tunable diode laser spectroscopy.

Regarding the pressure broadening studies for N_2O , Toth [3,4] reported results for the bands, $(\nu_1 + \nu_2 + \nu_3)$, ν_3 , $(\nu_1 + 2\nu_2)$, $2\nu_1$, $(\nu_2 + \nu_3)$, $(2\nu_2 + \nu_3)$, $(\nu_1 + \nu_3)$, $6\nu_2$, $3\nu_1$, $2\nu_3$, $(2\nu_1 + \nu_3)$, and $(\nu_1 + \nu_3)$ in the range of $2.1\text{-}5.6\text{ }\mu\text{m}$. Lacome *et al.* [5] reported the temperature dependence of the broadenings for the $(\nu_1 + 2\nu_2)$ and $2\nu_1$ bands at $4\text{ }\mu\text{m}$, and the ν_1 and $2\nu_2$ bands at $8\text{ }\mu\text{m}$. Nemotchinov *et al.* [6] presented the broadening coefficients and temperature dependence in the ν_3 band at $4.5\text{ }\mu\text{m}$ and expressed the J -dependence by empirical formulae. Yamada *et al.* [7] reported for the $(\nu_1 + \nu_3)$ band at $2.9\text{ }\mu\text{m}$ and proposed Padé approximants to present the J -dependence. Parkes *et al.* [8] reported for the $3\nu_3$ band at $1.5\text{ }\mu\text{m}$ at room temperature. In addition, several measurements have also been performed for the pure rotational transitions of N_2O in the $J = 1\text{-}0$ [9], $6\text{-}5$ [10], $9\text{-}8$ [11], $20\text{-}19$, $24\text{-}23$ [12], $22\text{-}21$, $23\text{-}22$ [13], $25\text{-}24$, and $26\text{-}25$ [14] transitions.

In the present study, we have measured the pressure broadening coefficients in the $3\nu_3$ band (1.52-1.53 μm) with various buffer gases (N_2 , O_2 , He, Ar, Ne, Kr and Xe) as a function of the rotational quantum number, and their temperature dependence (broadening exponent) with cavity ring-down spectroscopy (CRDS) using a tunable diode laser. CRDS is one of the sensitive spectroscopic absorption techniques for use with pulsed and continuous-wave (CW) lasers [15,16,17,18,19,20,21]. The high spectral resolution of diode lasers and CRDS makes precise measurement of pressure broadening possible. By applying an energy transfer model to the observed broadening coefficients for noble gases, the effective potential well depths at room temperature for $(\text{N}_2\text{O})_2$ as well as $(\text{CO}_2)_2$ have been experimentally evaluated and compared with theoretical calculations.

2. Experimental

The experimental setup used in the present study is similar with that described in a previous study.[22] An external cavity diode laser (Ando Electronics, AQ4321D, 1520-1620 nm, 6 mW, line width: 0.2 MHz) was used as the near-infrared light source. The output laser beam, deflected by an acousto-optical modulator (ISOMET, 1205-C2, 80 MHz), was directed into the optical cavity. The optical cavity consisted of two high reflectivity mirrors (II-VI Optics, reflectance > 0.999 , with 1 m radius of curvature and 7.8 mm diameter) with a separation of 60 cm. One of the two mirrors was incorporated in a tube-type Piezo actuator (Piezomechanik, HPSt 150/20) for cavity length modulation, with a rate of about 300 Hz. The transmitted light from the cavity was directed to an InGaAs photodiode detector (Hamamatsu Photonics, G5851-11) attached to a preamplifier (NF, SA220F5). When the transmitted beam reached a threshold level,

the deflected beam was switched off by the acousto-optical modulator crystal and the light stored within the cavity started to ring-down.

In the presence of an absorbing species the light intensity within the cavity is given by the expression.

$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma Nct) \quad (1)$$

where I_0 and $I(t)$ are the light intensities at time 0 and t , τ is the cavity ring-down time in the presence of an absorbing sample, τ_0 is the cavity ring-down time without the absorber present (typically 3 μ s), and c is the velocity of light. N and σ are the concentration and absorption cross section of the absorbing species, respectively.

The exponential decay data were digitized with an A/D converter (National Instruments, NI5112, 100 MHz, 8-bit, or NI5122 100 MHz, 14 bit) and processed using a LabVIEW software. Our program averaged the profile of several ring-down waveforms, for which individual ring-down decay curves except for the very initial part of the decay were fitted to a single-exponential function. Sixteen ring-down events were averaged for each spectral data point, thus, a complete scan took about 8 minutes.

Firstly, at room temperature (298 K) pressure broadening by various buffer gases (N_2 , O_2 , He, Ne, Ar, Kr, and Xe, 40-250 Torr) was measured at a fixed partial pressure of N_2O (0.30 Torr). Three or four measurements were performed at each pressure condition. The gases (except Kr and Xe) were flowed with use of mass-flow controllers (Kofloc, model 3660). Pressure and temperature of the sample gases in the cavity were monitored by pressure gauges (MKS, Baratron 622) and thermocouples at the monitor ports. Second, the temperature dependences of the pressure broadening by N_2 , and O_2 were measured for $P(3)$, $P(14)$ and $P(32)$ within the temperature range 243-353 K. Gas cooling and heating was achieved by flowing temperature-regulated

ethanol or water through the jacket of the glass cavity tube. To keep the temperature of the measurement region constant, the mirror mounts were supported within the cavity tube.

Theoretical calculations were performed using the GAUSSIAN 03 [23] suite of programs. Structures were determined using the unrestricted second-order Møller-Plessett [24,25,26] perturbation theory (UMP2). All energies reported were from full optimizations. The results presented here were those obtained using the 6-311+G(3df) basis set. Vibrational frequency calculations were performed using the UMP2/6-31G(d) level of theory. Zero-point energy corrections and entropy values used in determining the partition coefficients were based on these calculations. Geometries of isomers varied only slightly between basis sets used, so the difference in vibrational frequency due to difference in geometry using different basis sets would affect the calculated energies only slightly.

3. Results

Broadening coefficients at room temperature for various gases

The measured spectral profiles were analyzed with the Voigt function,

$$\frac{2 \ln 2}{\pi^{3/2}} \cdot \frac{W_L}{W_G^2} \cdot \int_{-\infty}^{\infty} \frac{e^{-t^2}}{(\sqrt{\ln 2} \cdot \frac{W_L}{W_G})^2 + (\sqrt{4 \ln 2} \cdot \frac{x - x_c}{W_G} - t)^2} dt \quad (2)$$

where x_c is the line-center frequency of the transition, W_G is the full-width at a half maximum (FWHM) of the Gaussian component, and W_L is the FWHM of the Lorentzian component. For the room temperature experiments, the Gaussian component was constrained to the room temperature Doppler width. In the present analysis, the line offset could not be determined. An example of the measured profile for the $P(3)$ at 6578.277 cm^{-1} , which was broadened by 200 Torr of N_2 , was shown in

the insert in Fig.1. The Voigt profile is shown by the solid curve. Thus, data obtained for the half-width at a half maximum (HWHM) of the Lorentzian component are plotted as a function of buffer gas pressure. A straight-line fit provides the pressure broadening coefficient, γ , in units of $\text{cm}^{-1}\text{atm}^{-1}$ as shown in Fig. 1. A small contribution ($\sim 2\%$) of self-broadening was taken into account with use of $\gamma(\text{N}_2\text{O})$, from 0.1186 for $P(3)$ to 0.0834 for $P(40)$, reported in the HITRAN data-base.[27]

The following index, m , is introduced to treat simultaneously the P - and R -branch transitions:

$$2m = J'(J' + 1) - J''(J'' + 1)$$

$$P\text{-branch } (J''-1 \leftarrow J'') \quad m = -J''$$

$$R\text{-branch } (J''+1 \leftarrow J'') \quad m = J'' + 1$$

If the rotational constants B'_v and B''_0 are approximately the same, then, m is proportional to the energy difference between the two rotational levels in the same vibrational band. Table 1 and Fig. 2 show the measured γ at room temperature. These data were fitted to the 1,1-Pad approximant in Table 2 and Fig. 2. [28]

$$\gamma(m) = \frac{a + b |m|}{1 + c |m|} \quad (3)$$

The values of γ decrease with $|m|$: a trend observed by our previous measurement and other groups conducting broadening measurements. [3-14,22] Based on the impact approximation, γ is expressed from the cross-sections in the terms of the Weiskopf radius, the number density of the collision partner, and the mean relative velocity of the collision partner. [29] The Weiskopf radius depends on the mean relative velocity and the C_6 coefficient of the Lennard-Jones potential for van der Waals broadening. Since inelastic collisions cause transitions between rotational levels, the

lines of low rotational quantum number, corresponding to rotational level separations less than $k_B T$, are broadened more than those of high rotational number where the level spacing is greater.

Temperature dependence of broadening coefficients

The results for changes in temperature can be expressed by the following equation:

$$\frac{\gamma(T)}{\gamma(T_0)} = \left(\frac{T}{T_0} \right)^{-n} \quad (4)$$

where n is temperature dependent exponent of the pressure broadening coefficient, and T_0 is 298 K in the present study.

Figure 3 shows the temperature plots for $P(32)$. With use of Equation 4, the values of n are thus obtained for N_2 and O_2 and are listed in Table 3 with the literature data. For $n(N_2)$ and $n(O_2)$, Lacome *et al.* [5] measured $n(N_2)$ and $n(O_2)$ for $|m| = 1-44$ for the $2\nu_1$ and $(\nu_1 + 2\nu_2)$ bands and reported n values using the average values for the $2\nu_1$ and $(\nu_1 + 2\nu_2)$ bands. Nemtchinov *et al.* [6] measured $n(N_2)$ and $n(O_2)$ for $|m| = 1-41$ for the ν_3 band. As listed in Table 3, our results obtained for the $3\nu_3$ band are close to the literature values for the $2\nu_1$, $(\nu_1 + 2\nu_2)$, and ν_3 bands [5,6].

4. Discussion

Comparison of the present data with other data

For the purpose of comparison, the $|m|$ -dependence of N_2 - and O_2 -broadening coefficients for the $3\nu_3$ band obtained in the present study are displayed in Fig. 4 along with the literature values for the ν_3 and $2\nu_3$ bands [4,6], and the pure rotational transitions [9-14]. Our results of the N_2 - and O_2 - broadening coefficients obtained for the $3\nu_3$ band are in good agreement with the most of the literature values listed above.

These results imply that the broadening coefficients are independent of vibrational level.

Theoretical γ values at 296 K were reported by Rohart *et al.* [13] using a semiclassical impact theory within the formulation proposed by Robert and Bonamy [30]. In their theory, the relaxation rate, $\Gamma(v_r)$, of the relative velocity, v_r , is given by

$$\Gamma(v_r) = n_M v_r \sum_{J_M} \rho_{J_M} \int_0^\infty S(b, v_r, J_M) 2\pi b db \quad (7)$$

where n_M is the number density of the collision partners, ρ_J is the relative population of collision partners to the J_M level in the fundamental vibrational state, S is the complex differential cross-section representing the collisional efficiency, and b is the impact parameter. They computed the broadening parameters, γ , for the mean relative velocity, $\langle v_r \rangle$. The $|m|$ -dependence of γ is plotted in Fig. 4 for the purpose of comparison with the experimental data. The solid curves in Fig. 4 indicate their theoretical results for the total collisional interaction potential that involved the atom-atom Lennard-Jones interactions in addition to electronic interactions of dipole, quadrupole, octopole, and hexadecapole. The dashed curves in Fig. 4 indicate their results for the same potential in which the octopole, and hexadecapole contributions were omitted. Our experimental results are in agreement with their theoretical values for both N_2 - and O_2 - broadening coefficients except only for the N_2 - broadening coefficients at high $|m|$ values ($|m| \geq 30$).

Estimate of effective potential energy well depths for dimers

The potential well depth for dimers has been evaluated using the observed broadening coefficients for noble gases. Barry *et al.* [31] measured broadening coefficients for the $2\nu_5$ band of CH_2O and firstly adapted the Permenter-Seaver's model

for pressure broadening to estimate the binding energy of $(\text{CH}_2\text{O})_2$. Permenter and Seaver [32,33] have developed a successful model that correlates Boltzmann averaged cross sections, σ_M , of a variety of energy transfer processes for a variety of collision partners, M, with the intermolecular well depths, ϵ_{AM} , for the interaction between the molecule, A, and a collision partner, M.

$$\sigma_M = C \exp(\epsilon_{AM}/k_B T) \quad (8)$$

where C is a constant, k_B is Boltzmann's constant, and T is temperature. The correlation is particularly useful for energy transfer processes which depend upon long range attractive forces. In the Lorentz-Berthelot geometric mean approximation, $\epsilon_{AM} = (\epsilon_{AA} \epsilon_{MM})^{1/2}$, the equation is conveniently expressed in terms of the well depth, ϵ_{AA} , for the dimer of A, and ϵ_{MM} for the dimer of M,

$$\ln(\sigma_M) = \ln C + \beta(\epsilon_{MM}/k_B)^{1/2} \quad (9)$$

where β is given by

$$\beta = (\epsilon_{AA}/k_B T^2)^{1/2} \quad (10)$$

Figure 5 shows the Permenter-Seaver plots for the pressure broadening of the $P(3)$ transition of the N_2O $3\nu_3$ band obtained in our experiment for a variety of colliding rare gases ($\epsilon_{\text{HeHe}}/k_B = 10.99$, $\epsilon_{\text{NeNe}}/k_B = 42.31$, $\epsilon_{\text{ArAr}}/k_B = 143.33$, $\epsilon_{\text{KrKr}}/k_B = 201.43$, and $\epsilon_{\text{XeXe}}/k_B = 282.88$ K). These ϵ_{MM}/k_B data are taken from the theoretical values summarized by Tang *et al.* [34]. In Fig. 5, σ_M is the cross section for the broadening process calculated by converting γ to SI units and multiplying by the factor $2\pi k_B T / \langle v_r \rangle$. As shown in Fig. 5, a linear correlation is observed except the data for He. It may be attributed that the Lorentz-Berthelot geometric mean approximation does not hold for the case of He. This result is consistent with the previous reports that the rule of Permenter-Seaver is poor when He is one of the collision partners [35,36], since

$\epsilon_{\text{HeHe}}/k_B$ is too small compared with ϵ_{AA}/k_B . Linear least-squares fit analysis of the data except for He in Fig. 5 yielded the well depth for $(\text{N}_2\text{O})_2$ to be $\epsilon_{\text{N}_2\text{O}-\text{N}_2\text{O}}/k_B = 614 \pm 116$ K. The Permenter-Seaver's model is also applied for the pressure broadening of the $R(0)$ transition of the CO_2 $(3\ 0^0\ 1)_{\text{III}} \leftarrow (0\ 0\ 0)$ band obtained in our previous study [22] as shown in Fig. 5. Linear least-squares fit analysis of the data except the data for He yielded the well depth for $(\text{CO}_2)_2$ to be $\epsilon_{\text{CO}_2-\text{CO}_2}/k_B = 472 \pm 43$ K.

In the present study, the structures and relative energies of $(\text{N}_2\text{O})_2$ have been calculated using the UMP2/6-311+G(3df) level of theory. Four structures were found for $(\text{N}_2\text{O})_2$, shown in Fig. 6. Vibrational frequencies calculated verified that these were true minima. Optimized geometries, vibrational frequencies, and rotational constants for these dimers can be found in the supplemental information Tables. Well depths (D_e) of the four N_2O dimer structures calculated here are all close to each other, ranging from 904 to 1027 K ($1.80 - 2.04$ kcal mol⁻¹). The thermodynamic parameters for the four structures reported here are shown in Table 4. The zero-point energy (ZPE) were calculated using the UMP2/6-31G(d) level of theory. Applying the ZPE correction to these structures, results in a binding energy (D_0) ranging from 748-872 K. This leads to an enthalpy for dimerization (ΔH_{298}) for the four structures I, II, III and IV of 716 K, 612 K, 723 K, and 583 K, respectively. Partition coefficients (K_{eq}) of formation of the dimers have been calculated from our theoretical thermodynamic values from 220 – 298 K, and can be found in the supplemental information tables. Enthalpy and entropy values used are listed in Table 4. As can be seen, the difference in entropy between the N_2O dimer structures influences which structure is favored greatly. The K_{eq} values at 298 K for structures I, II, III and IV of the N_2O dimer are 5.3×10^{-24} , 8.3×10^{-24} , 6.9×10^{-24} , 2.0×10^{-23} cm³ molecule⁻¹, respectively.

These calculations are in general agreement with previous studies. We find these four isomers of the N_2O dimer to be true minima. This was also seen in a recent work by Valdés and Sordo [37]. They analyzed the potential energy surface of $(\text{N}_2\text{O})_2$ at the MP2 level of theory using aug-cc-pVDZ and cc-pVTZ basis sets. They reported that three slipped parallel configurations were characterized as minima with dissociation energies ranging from 816 to 880 K and from 632 to 693 K for the theory using aug-cc-pVDZ and cc-pVTZ basis set, respectively. They suggested that T-shaped structures probably correspond to the transition structures connecting the slipped parallel structures. However, our calculations show that the thermodynamically favored structure is T-shaped, albeit slightly.

In the computational studies, the well depth was generally calculated for the minimum energy geometry, while our experimental results are obtained for an average over the different orientations of the two colliding N_2O molecules. From the weighted average of the well depth for each configuration, I, II, III and IV, the effective well depth of $(\text{N}_2\text{O})_2$ have been evaluated to be $\epsilon_{\text{N}_2\text{O}-\text{N}_2\text{O}}/k_B = 821$ K where the existing possibility of the each configuration was estimated using K_{eq} values at 298 K. The results were plotted in Fig. 5 with dashed line that has a slope which corresponds to the effective well depth of $\epsilon_{\text{N}_2\text{O}-\text{N}_2\text{O}}/k_B = 821$ K. The experimental result, $\epsilon_{\text{N}_2\text{O}-\text{N}_2\text{O}}/k_B = 614 \pm 116$ K is slightly smaller than the theoretical results of 821 K. This difference may be caused by two reasons. One reason is that the intermolecular well depth, ϵ_{AM} , in equation (8) is in reality only proportional to the true well depth. Lin *et al.* [32] reported that the well depth in eq. (8) and the true well depth could lie within a factor of 2 for model collision calculations using assumed well depths for Lennard-Jones potentials. The other reason is possible errors in our theoretical calculations

particularly due to ZPE and ΔS . Those are dependent on harmonic vibrational frequencies. Because of this, ZPE is really an upper limit, and ΔS may be slightly off the experimental value. Since $(\text{N}_2\text{O})_2$ is such a weakly bound complex, these errors could be significant in this case.

It is interesting to compare the well depth of $(\text{N}_2\text{O})_2$ with isoelectronic $(\text{CO}_2)_2$. N_2O and CO_2 have identical molecular weight, and similar electronic charge distribution, that is, polarizability and electric moment. Since N_2O has a static dipole moment (0.16 D), the well depth of $(\text{N}_2\text{O})_2$ is larger than that of $(\text{CO}_2)_2$. We have performed theoretical calculations for $(\text{CO}_2)_2$. Only one true minima was found for $(\text{CO}_2)_2$, shown in Fig. 6. The optimized geometry, vibrational frequencies, and rotational constants for the dimer can be found in the supplemental information Tables. The well depth (D_e) for the lone structure was calculated to be 792 K. The binding energy (D_0) is 642 K, while the enthalpy of dimerization (ΔH_{298}) is 486 K. These results are shown in Table 4. The equilibrium constant for the formation of the CO_2 dimer is $4.4 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K. For the well depth, Tsuzuki et al. [38] calculated the energy profile of the lowest path connecting the slipped-parallel (C_{2h}) and T-shaped (C_{2v}) dimers of CO_2 using a 6-311+G(2df) basis set with the MP2 level electron correlation correction and with the counterpoise correction. They showed that there is no inversion barrier between the two slipped-parallel dimers and T-shaped dimer and that T-shaped dimer is transition state connecting the two stable slipped-parallel dimers. They reported interaction energies of the slipped-parallel and T-shaped $(\text{CO}_2)_2$ to be 649 and 539 K, respectively. Bock et al. [39] reported that the global maximum well depth, of approximately 695 K, occurs for the slipped-parallel configuration based on three intermolecular potentials employed by Steinebrunner et al.,

[40] Bukowski et al., [41] and Bock et al. [42]. In our calculations, we find that the T-shaped isomer is a transition state, and that the slipped-parallel isomer is the only true minimum for the CO₂ dimer. The present experimental result, $\epsilon_{\text{CO}_2\text{-CO}_2}/k_B = 472 \pm 43$ K, is again smaller than the theoretical results of $\epsilon_{\text{CO}_2\text{-CO}_2}/k_B = 642$ K. The dashed line in Fig. 5 has a slope that corresponds to the effective well depth of $\epsilon_{\text{CO}_2\text{-CO}_2}/k_B = 642$ K.

Pressure broadening data for air

From the data reported herein, the air broadening coefficient $\gamma(\text{air})$ for N₂O is estimated. We calculate $\gamma(\text{air})$ using the relation: $\gamma(\text{air}) = 0.79\gamma(\text{N}_2) + 0.21\gamma(\text{O}_2)$. Table 5 compares the present $\gamma(\text{air})$ values with the reported values for 3 ν_3 by Parkes *et al.*[8], and also the HITRAN data-base [27] that are taken from Toth [4] for the ($\nu_1 + \nu_2 + \nu_3$), ν_3 , ($\nu_1 + 2\nu_2$), $2\nu_1$, ($\nu_2 + \nu_3$), ($2\nu_2 + \nu_3$), ($\nu_1 + \nu_3$), $6\nu_2$, $3\nu_1$, $2\nu_3$, ($2\nu_1 + \nu_3$), and ($\nu_1 + \nu_3$) bands, Lacome *et al.* [5] for the $2\nu_1$, ($\nu_1 + 2\nu_2$), ν_1 , and $2\nu_2$ bands, and Nemtchinov *et al.* [6] for ν_3 band. The present $\gamma(\text{air})$ values are in good agreement with the HITRAN data-base, but smaller than the values by Parkes *et al.*[8]. From the temperature dependence of $0.79\gamma(\text{N}_2) + 0.21\gamma(\text{O}_2)$, the temperature dependence parameter, n , was estimated to be 0.73(11) for $P(4)$, 0.79(23) for $P(14)$, and 0.76(12) for $P(32)$. Our results are in good agreement with the values of 0.75 in the HITRAN data-base.

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Table 1. Buffer-gas pressure broadening coefficients, γ , in the unit of $\text{cm}^{-1}\text{atm}^{-1}$ for N_2O at 298 K ^a

$ m $	N_2	O_2
3	0.092(2)	0.081(3)
4	0.087(2)	0.082(2)
6	0.085(1)	0.079(2)
7	0.085(1)	0.077(1)
8	0.086(2)	0.076(2)
9	0.084(2)	0.075(1)
10	0.081(2)	0.075(3)
14	0.081(4)	0.071(4)
18	0.088(3)	0.065(2)
23	0.075(2)	0.064(2)
32	0.066(1)	0.060(1)
40	0.065(1)	0.056(1)

$ m $	He	Ne	Ar	Kr	Xe
3	0.070(3)	0.058(2)	0.079(3)	0.080(1)	0.085(1)
8	0.065(2)	0.049(2)	0.072(3)		
15	0.061(2)	0.038(3)	0.063(2)		
26	0.054(2)	0.041(3)	0.052(1)		

^a Numbers in parentheses are one standard deviation obtained by the straight line fitting in units of the last digits quoted.

Table 2. Parameters for the 1,1-Pad approximant in Equation 3

Buffer gas	a	b	c
N ₂	0.091	0.000	0.011
O ₂	0.088	0.001	0.038
He	0.072	0.000	0.017
Ne	0.069	0.006	0.168
Ar	0.084	-0.001	0.012

Table 3. Temperature dependent parameters, $n(\text{N}_2)$ and $n(\text{O}_2)$.^a

$n(\text{N}_2)$			
$ m $	this work ^b	Lacome <i>et al.</i> ^c	Nemtchinov <i>et al.</i> ^d
4	0.75(10)	0.78(05)	0.74(14)
14	0.78(27)	0.72(05)	0.72(14)
32	0.78(11)	0.79(05)	0.78(14)

$n(\text{O}_2)$			
$ m $	this work ^b	Lacome <i>et al.</i> ^c	Nemtchinov <i>et al.</i> ^d
4	0.65(14)	0.88(05)	0.76(14)
14	0.85(07)	0.86(05)	0.72(14)
32	0.69(14)	0.95(05)	0.80(14)

a Numbers in parentheses are one standard deviation in units of the last digits quoted.

b This work for the $3\nu_3$ band.

c Ref. 5 for the $2\nu_1$ and $(\nu_1 + 2\nu_2)$ bands.

d Ref. 6 for the ν_3 band.

Table 4 Pressure broadening coefficients for air^a

$ m $	this work ^b	Parkes <i>et al.</i> ^c	HITRAN ^d
3	0.089(02)	0.139(10)	0.0916
4	0.086(02)	–	0.0901
5	–	0.103(08)	0.0887
6	0.084(01)	–	0.0874
7	0.083(01)	–	0.0861
8	0.084(02)	0.097(10)	0.0849
9	0.082(02)	–	0.0838
10	0.079(02)	–	0.0827
14	0.079(04)	–	0.0790
15	–	0.091(05)	0.0782
18	0.075(03)	–	0.0761
21	–	0.088(11)	0.0743
23	0.075(02)	–	0.0734
26	–	0.091(15)	0.0722
32	0.065(01)	–	0.0707
34	–	0.086(15)	0.0703
40	0.063(01)	–	0.0696

a Numbers in parentheses are one standard deviation obtained by the straight line fitting in units of the last digits quoted.

b This work for the $3\nu_3$ band.

c Ref. 8 for the $3\nu_3$ band.

d Ref. 27. Those data in HITRAN data base are taken from Ref. 4 for the $(\nu_1 + \nu_2 + \nu_3)$, ν_3 , $(\nu_1 + 2\nu_2)$, $2\nu_1$, $(\nu_2 + \nu_3)$, $(2\nu_2 + \nu_3)$, $(\nu_1 + \nu_3)$, $6\nu_2$, $3\nu_1$, $2\nu_3$, $(2\nu_1 + \nu_3)$, and $(\nu_1 + \nu_3)$ bands, Ref. 5 for the $2\nu_1$, $(\nu_1 + 2\nu_2)$, ν_1 and $2\nu_2$ bands, and Ref. 6 for the ν_3 band.

Table 5: Theoretical thermodynamic values for (N₂O)₂ and (CO₂)₂

Dimer	Structure	D_e (K)	D_0 (K)	ΔH_{298} (cal mol ⁻¹)	ΔS_{298} (cal mol ⁻¹ K ⁻¹)
(N ₂ O) ₂	I	1006	856	-1420	-18.0
	II	922	774	-1220	-16.4
	III	1027	872	-1440	-17.5
	IV	904	748	-1160	-14.5
(CO ₂) ₂	I	792	642	-966	-16.8

Figure captions

Fig. 1. Lorentzian widths (HWHM) for the $P(3)$ transition at 298 K as a function of pressure of buffer gases. Error bars indicate one standard deviation determined by the profile-fit procedure. ■: N₂, ●: O₂, ▲: He. The inset shows an absorption profile for the $P(3)$ transition of N₂O broadened by 200 Torr of N₂ at 298 K. Filled circles represent experimental data. The solid curve represents a calculated spectrum with the Voigt function.

Fig. 2. 1,1-Pad approximant plots at 298 K using Equation 3: Pressure broadening coefficient, γ , as a function of the rotational level, $|m|$. As for $|m|$, see text. Error bars indicate one standard deviation determined by the profile-fit procedure.

Fig.3. Temperature dependence of the pressure broadening coefficients for the $P(32)$ transition. ■: N₂, ●: O₂. Error bars indicate one standard deviation determined by the profile-fit procedure.

Fig. 4. $|m|$ dependence of line broadening parameters of N₂O in collisions with N₂ (upper panel) and O₂ (lower panel). Experimental results: $3\nu_3$ (●, This work), ν_3 (▲, [6]), and $2\nu_3$ (■, [4]) bands, and pure rotational transitions (▼, [9-14]). Theoretical results reported by Rohart et al. [13]: total potential involving the atom-atom Lennard-Jones interactions in addition to electronic interactions of dipole, quadrupole, octopole, and hexadecapole (solid curves) or by neglecting in the electrostatic potential

the octopole and hexadecapole moment of the absorber and the perturbers (dashed curves). Error bars indicate one standard deviation values of the measurements.

Fig. 5. Plots of the logarithm of the cross section σ_M for the broadening process of $P(3)$ transition of the N_2O $3v_3$ band obtained in our experiment, and the $R(0)$ transition of the CO_2 $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band obtained in the present study [22] *versus* the well depth, ϵ_{MM} , of the dimer of a variety of noble gases (○: He, ●: Ne, Ar, Kr, and Xe). Error bars indicate one standard deviation values of the measurement. Solid lines show the results of a linear least square fit of the experimental data except for He (see text). Dashed lines show the results of our theoretical calculations.

Fig. 6. Optimized structures for $(N_2O)_2$ and $(CO_2)_2$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

$(\text{N}_2\text{O})_2$ Structure I

$(\text{N}_2\text{O})_2$ Structure II

$(\text{N}_2\text{O})_2$ Structure III

$(\text{N}_2\text{O})_2$ Structure IV

$(\text{CO}_2)_2$ Structure I

Figure 6

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