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Isotope effects in the infrared spectra of the polar and nonpolar isomers of N_2O dimer

M. Dehghany, Mahin Afshari, Z. Abusara, C. Van Eck, N. Moazzen-Ahmadi *

Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alta., Canada T2N 1N4

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Abstract

The rotationally resolved spectra of $^{15}N^{15}N^{16}O$ dimer for the polar and nonpolar isomers are studied in the region of the N–N stretching fundamental of the monomer ($\sim$2150 cm^{-1}) using a rapid-scan tunable diode laser spectrometer to probe a pulsed supersonic jet expansion. These spectra are very similar to the corresponding spectra of the normal species, $(^{14}N^{14}N^{16}O)_2$. Structural parameters and vibrational shifts obtained here are compared with those of the normal species and ab initio values. These results confirm that the nonpolar isomer has a centrosymmetric slipped-antiparallel structure while the polar isomer consists of two slipped and (approximately) parallel monomer units.

Keywords: N_2O dimer; Ro-vibrational spectrum; Clusters; Laser spectroscopy; Pulsed supersonic jet; Isotope effects

1. Introduction

N_2O dimer has been subject of many studies since supersonic jet expansion became a reliable source to form weakly bound van der Waals complexes [1–3]. Miller et al. [4,5] reported the first observation of nitrous oxide dimer in the region of N_2O $\nu_1 + \nu_3$ combination band (around 3500 cm^{-1}). They showed that the dimer has a planar centrosymmetric structure with two monomers in a slipped-antiparallel configuration (C_{2h} symmetry). This structure was subsequently confirmed by Qian et al. [6] and Ohishima et al. [7], who studied two further infrared bands in the regions of N_2O ν_1 ($\sim$2220 cm^{-1}) and ν_3 ($\sim$1280 cm^{-1}) fundamentals, respectively. Later, ab initio calculations by Valdes and Sordo [8] found that the slipped-antiparallel structure with O atoms occupying the inner position is indeed the lowest energy isomer. We have extended the study of N_2O dimer in the region of ν_1 fundamental band by assigning more transitions (200 vs. 130 lines) and covering a wider spectral range (4.7 vs. 3 cm^{-1}) [9]. Because of its center of symmetry, the C_{2h} isomer is nonpolar and cannot be studied by microwave spectroscopy.

The potential energy surface explored by Valdes and Sordo [8] had six stationary points, with three minima at all levels of theory. The second lowest energy isomer was found to be polar with a slipped parallel geometry. We recently observed an infrared spectrum in the N_2O ν_1 fundamental region, which we assigned to the polar N_2O dimer having C_s symmetry [9]. Although the pure rotational spectrum of this isomer is detectable in the microwave region, this spectrum is considerably complicated because of the presence of quadrupole hyperfine splittings from the four in-equivalent ^{14}N nuclei in the normal isotopomer [10].

The structural parameters of the nonpolar and polar N_2O dimers are very similar, but their molecular symmetries are completely different. In the nonpolar form, the two monomers are equivalent, so the vibrational mode corresponding to the in-phase N–N vibration is infrared inactive. In the case of the polar isomer, the two monomer units are no longer equivalent and both in-phase and out of phase vibrations are infrared allowed. To date, only one of the two allowed bands has been detected. The band

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* Corresponding author. Fax: +1 403 289 3331.
E-mail address: ahmadi@phas.ucalgary.ca (N. Moazzen-Ahmadi).

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reported in Ref. [9] probably belongs to the stronger in-phase vibration. The weaker out of phase vibration band has not been detected yet and the situation is similar to that of OCS polar dimer [11].

In the present work, we expand the analysis of the normal isotopomer of the polar and nonpolar N_2O dimer, $(^{14}N^{14}N^{16}O)_2$, by assigning more rotational transitions. We also report for the first time the observation of the N–N stretching fundamental for both nonpolar and polar isomers of $(^{15}N^{15}N^{16}O)_2$. Structural parameters obtained from the normal and ^{15}N substituted isotopomer are compared with those predicted by ab initio calculations. Microwave study of the isotopologues of the polar N_2O dimer would be very helpful in determining a more exact structure of this isomer including the angle between the two monomer axes.

2. Experimental details

The spectra were observed by direct infrared absorption using a pulsed supersonic jet and a tunable diode laser. The laser was used in a rapid-scan signal averaging mode [12,13]. Simultaneous etalon (with a free spectral range of $0.00997\ cm^{-1}$) and $^{14}N_2O$ reference gas spectra were recorded to perform a frequency interpolation and absolute calibration, respectively. A dilute gas mixture of N_2O ($\sim$0.5%) in He was used with a backing pressure of 7.8 atm. Detailed description of experimental setup and data acquisition system were published previously [14].

A somewhat higher signal to noise ratio was achieved by using a multi-channel slit which distributes the gas across the slit nozzle, enhancing cluster formation as well as increasing absorption path length by approximately a factor of 2 compared to our previous slit (30 mm vs. 14 mm). In addition to better signal to noise, this slit provides narrower absorption line width ($\sim 0.0013\ cm^{-1}$). Detailed description of the multi-channel slit has been given in Ref. [15]. We used isotopically enriched sample of $^{15}N^{15}N^{16}O$, obtained from Iconisotopes, with a stated atomic purity of 99%.

3. Results and analysis

3.1. Spectra of the nonpolar $(^{14}N^{14}N^{16}O)_2$ and $(^{15}N^{15}N^{16}O)_2$

The number of assigned transitions reported in our previous work [9] for the nonpolar $(^{14}N^{14}N^{16}O)_2$ was 208 with the rotational levels up to $J = 11$ and $K_a = 4$. The improved signal to noise and narrower line width resulting from the use of the multi-channel slit allowed us to assign 58 additional transitions thus extending the rotational quantum numbers to $J = 12$ and $K_a = 5$. Fig. 1 shows a comparison of the observed spectrum recorded using the multi-channel slit (middle trace) and our previous slit (upper trace) together with the simulated spectrum at 2.0 K (lower trace). For line measurement, simulation and fitting, we used Colin Western's PGopher program [16], but final fits were made using a program kindly provided by ARW McKellar [12] and a conventional asymmetric rotor Hamiltonian in the a-reduction form [17]. Fits were made including all quartic centrifugal distortion parameters, except for δ_K which was set to zero. Δ_{JK} was still poorly determined, even though the fit covered a wider range of J and K_a and a larger number of transitions. It was difficult to know which of the parameters should be varied. Eventually, we decided to fix the upper state distortion parameters to their corresponding values for the lower state and Δ_{JK} equal its value for $(^{15}N^{15}N^{16}O)_2$. See below. The molecular parameters resulted from the fit are given in column 2 of Table 1 and are compared with results from our previous study [9]. The observed line positions are listed in Table A-1 of the Appendix.

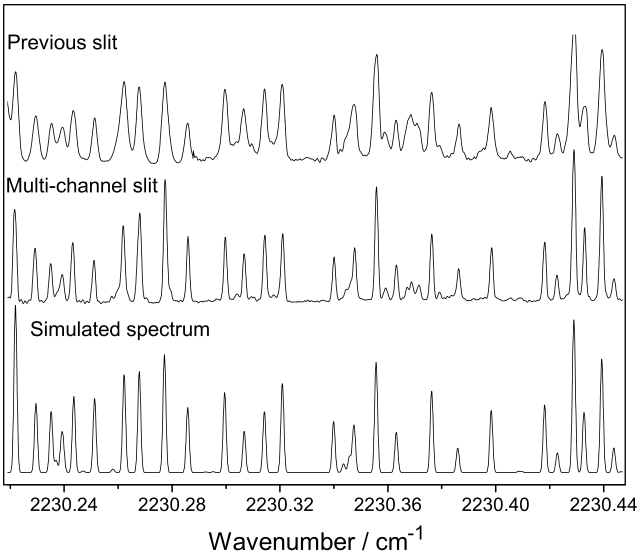

Fig. 1. Comparison of corresponding regions in the observed spectra of the nonpolar $(^{14}N^{14}N^{16}O)_2$ recorded with the multi-channel slit (middle trace) and our previous slit nozzle (upper trace) together with the simulated spectrum at 2.0 K (lower trace). Missing regions are regions of strong N_2O monomer or He–N_2O absorption.

The band for the nonpolar $(^{15}N^{15}N^{16}O)_2$ was easily located based on the monomer band origins. The observed spectrum of $(^{15}N^{15}N^{16}O)_2$ was very similar to that of the normal isotope with a pattern being slightly more compressed as expected due to its greater mass and hence smaller rotational parameters. As with $(^{14}N^{14}N^{16}O)_2$, the spectrum consists of equal intensity contributions from a-type and b-type transitions. Fig. 2 shows a portion of the observed (upper trace) and simulated (lower trace) spectra. We assigned 333 transitions for the nonpolar $(^{15}N^{15}N^{16}O)_2$ with values of J up to 12 and K_a up to 5. These are listed in Table A-2 of the Appendix. The number of transitions and the ranges for J and K_a were sufficient to vary ν_0, A, B, and C, for the lower and upper states and the distortion parameters (save δ_K) for the lower state. The upper state distortion parameters were set to their values for the lower state. Molecular parameters obtained from this fit are listed in column 4 of Table 1.