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Rovibrational Energy Levels and Photoabsorption Spectra of the Isotopically Substituted N_2O: A Theoretical Study

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ABSTRACT The rovibrational spectra of the ground electronic state potential energy surface, X^1A', for the $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{15}N^{15}N^{16}O$, $^{14}N^{14}N^{17}O$ and $^{14}N^{14}N^{18}O$ isotopomers have been calculated variationally by fixing the total angular momentum at $J = 0$ with parity state either even or odd, and $J = 1$ with odd parity state. Theoretical results show good agreement with the experimental observations for the three lowest vibrational states namely $(0, 0^0, 0)$, $(0, 1^1, 0)$ and $(0, 2^0, 0)$ with maximum discrepancy of 20.95 cm^{-1}. Using the ground state wavefunctions of the five heavy isotopomers and the corresponding transition dipole moments connecting to the three lowest singlet excited state potential energy surfaces ($2^1A'$, $1^1A''$ and $2^1A''$), the resulting theoretical absorption spectra show in excellent agreement with the experimental spectra.

ABSTRAK Spektrum putaran getaran bagi keadaan asas permukaan tenaga keupayaan elektronik, X^1A', untuk isotopomer-isotopomer , $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{15}N^{15}N^{16}O$, $^{14}N^{14}N^{17}O$ dan $^{14}N^{14}N^{18}O$ telah dikira secara variasi dengan menetapkan jumlah momentum sudut pada $J = 0$ dengan keadaan pariti genap atau ganjil, dan $J = 1$ dengan keadaan pariti genap. Keputusan teori menunjukkan persetujuan yang baik berbanding dengan pemerhatian eksperimen untuk tiga keadaan getaran terendah iaitu $(0, 0^0, 0)$, $(0, 1^1, 0)$ dan $(0, 2^0, 0)$ dengan perbezaan maksimum 20.95 cm^{-1}. Dengan menggunakan fungsi gelombang dari lima isotopomer berat and pemindahan momen berkutub yang menghubungkan kepada tiga keadaan terendah permukaan tenaga keupayaan singlet ($2^1A'$, $1^1A''$ dan $2^1A''$), hasilan spektrum-spektrum penyerapan teori menunjukkan persetujuan yang sangat baik dengan spektrum-spektum eksperimen.

(Variational, potential energy surfaces, Jacobi coordinate, rovibrational energy, ultraviolet spectrum, time-dependent wavepacket, isotopomer)

INTRODUCTION

Nitrous oxide (N_2O) is a prominent greenhouse gas which also plays an important role in the ozone depletion. It is emitted into the atmosphere from natural and anthropogenic sources including the oceans, soil, the combustion of fuels, biomass burning, the use of fertilizer, catalytic converters for automobiles and various industrial processes [1, 2]. It is removed from the atmosphere mainly by photolysis in the stratosphere. Of the three important biologically mediated greenhouse gases, our understanding of the isotopic budget of N_2O lags far behind that of carbon dioxide and methane [3, 4]. Efforts have been made to investigate the isotopic fractionation of N_2O in various production and loss processes [3 – 9]. These measurements reveal that, relative to tropospheric N_2O, the major biological sources of N_2O are light in both ^{15}N and ^{18}O, while stratospheric N_2O is found to be isotopically heavy. In an effort to explain the heavy stratospheric N_2O, Yung and Miller [10] proposed a wavelength-dependent enrichment mechanism during ultraviolet photolysis. They suggested that the difference in the zero point vibrational energy for the heavier N_2O isotopomers causes a blue-shift in the ultraviolet absorption spectrum, resulting in fractionation. Analogous to determining the kinetic fractionation for a chemical reaction, the photolytic fractionation factor will be equal to the ratio of the heavy to light cross sections

$$\alpha = \frac{\sigma_{\text{heavy}}}{\sigma_{\text{light}}}$$

where the lightest isotope is $^{14}N^{14}N^{16}O$. Interest in the characterization of the vibration-rotation spectra of the N_2O isotopomers has been renewed as well in recent years due to the observation in the stratosphere of unexpected mass-independent isotopic enrichments and to the spectroscopic studies of these molecular species carried out in condensed phases.

This paper presents the results of calculations of the rovibrational energy levels of the ground electronic state and the results of the photoabsorption spectra in the first absorption band for five most importantly heavy isotopomers of N_2O. Comparison is made between the theoretical calculations and the available experimental results.

THEORY

We studied theoretically the vibrational spectrum of the five rare isotopomers by performing exact variational calculations of its rovibrational energies and wavefunctions. The details of the theory and computer procedures have been described in our paper appearing in this journal [11]. In the present calculations, we employed the previous computed ground state potential energy surface X^1A' [11] which should be isotopically invariant according to the Born-Oppenheimer approximation. In solving the nuclear motion, we used a non-symmetric form of the Jacobi coordinates for the calculations of $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ isotopomers where the center of mass of the N-N fragment is no longer at the center of the bond.

We employed the time-dependent quantum wavepacket methods to interpret the photoabsorption spectrum of N_2O in terms of the nuclear motion on the upper electronic potential surfaces namely $2^1A'$, $1^1A''$ and $2^1A''$. The details information about the surfaces can be referred through reference [12]. The time-dependent version of the total photoabsorption cross section is given by [13, 14]

$$\sigma_{\text{tot}}(E) = \frac{2\pi^2\nu}{\hbar c\epsilon_0}\int_{t=0}^{t=\infty} \exp\left(\frac{\mathrm{i}Et}{\hbar}\right)\langle\Phi(t=0)\,|\Phi(t)\rangle\, dt.$$

where E is the final energy which is related to the energy of the ground electronic state E_i as $E = h\nu + E_\mathrm{i}$, and $\Phi(t=0)$ is the initial wave packet at time $t = 0$ which is given by

$$\Phi(t=0) = \vec{\epsilon}.\vec{\mu}\psi_\mathrm{i}$$

where ψ_i is the nuclear wavefunction (refer [11]) for the ground electronic state potential with energy E_i and $\vec{\mu}$ is the electronic transition dipole moment connecting two different electronic states. In the excited state, Φ is not a stationary state and it evolves as $\Phi(t)$ according to the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial\Phi(t)}{\partial t} = \hat{H}\Phi(t)$$

where $\hat{H}$ is the full upper surface Hamiltonian (refer [11]) for nuclear motion. By solving equation (1), the wave packet at time $t > 0$ is obtained as

$$\Phi(t) = \exp\left(\frac{\mathrm{i}\hat{H}t}{\hbar}\right)\Phi(t=0).$$

Thus, the overlap of $\Phi(t)$ with$\Phi(t=0)$, Fourier transformed, gives the spectrum. Once $\langle\Phi(t=0)\,|\Phi(t)\rangle$ is known, the photoabsorption cross section at all frequencies can be trivially obtained.

We studied the contribution to the total absorption cross section from the initial state in (0, 0^0, 0), (0, 1^1, 0) and (0, 2^0, 0) modes at temperature of 233 K. A Boltzmann average over initial vibrational states is given by the following equation

$$\sigma(T) = \frac{\sigma_{000} + 2\sigma_{010}e^{\Gamma_{010}} + 3\sigma_{020}e^{\Gamma_{020}}}{1 + 2e^{\Gamma_{010}} + 3e^{\Gamma_{020}}}$$

where

$$\Gamma_{ijk} = \frac{-\epsilon_{ijk}}{kT}$$

with k is Boltzmann constant, T is temperature in Kelvin, ϵ is vibrational energy of the ground state and the coefficients 1, 2 and 3 are used to account for the degeneracy of the states (0, 0^0, 0), (0, 1^1, 0) and (0, 2^0, 0).

The total photoabsorption cross section for N_2O is constructed from the sum over Boltzmann averaged absorption line shapes of the three lowest excited states $2^1A'$, $1^1A''$ and $2^1A''$ which is given by

$\sigma_{total} = \sigma_{2^1A'} + \sigma_{1^1A''} + \sigma_{2^1A''}$

RESULTS AND DISCUSSIONS

The dynamics calculations were performed on the personal computer consisting of 2.4 GHz Intel Pentium Core 2 Duo CPU with 2.0 GB RAM. There are five species of interest when analyzing the rare N_2O isotopomers namely $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{15}N^{15}N^{16}O$, $^{14}N^{14}N^{17}O$ and $^{14}N^{14}N^{18}O$. The predicted and observed vibrational energies for these isotopomer are given in tables 1 - 5. In general, for those isotopomers for which there is sufficient experimental information to make a relevant comparison, the agreement between calculated and observed values is good, especially for the $^{14}N^{14}N^{17}O$ isotopomer with the maximum discrepancy of 26.91 cm^{-1} arising from the state (3, 0^0, 0). The maximum discrepancy for other isotopomers are: 53.88 cm^{-1} (2, 4^0, 0) for $^{15}N^{14}N^{16}O$; 28.52 cm^{-1} (1, 0^0, 0) for $^{14}N^{15}N^{16}O$; 30.72 cm^{-1} (2, 2^0, 0) for $^{15}N^{15}N^{16}O$; 26.91 cm^{-1} (3, 0^0, 0) for $^{14}N^{14}N^{17}O$ and 36.76 cm^{-1} (2, 1^1, 0) for $^{14}N^{14}N^{18}O$. Moreover, for the three lowest vibrational states, i.e., (0, 0^0, 0), (0, 1^1, 0) and (0, 2^0, 0), the maximum discrepancy of 20.95 cm^{-1} comes from the state (0, 2^0, 0) of the $^{14}N^{14}N^{18}O$ isotopomer and accordingly, the ground state wavefunctions should be of sufficient quality to be used to study the isotopic effects in the $N_2O(X^1\Sigma^+) \rightarrow N_2(X^1\Sigma_g^+) + O(^1D)$ photodissociation process.

Figure 1 displays the absorption spectra corresponding to temperatures of 233 K, for several selected isotopomers over the region of banded structures between 174 and 188 nm, and a smooth continuum absorption region between 195 and 210 nm where the bulk of the stratospheric N_2O photolysis takes place. The right shoulder of the absorption spectra between 184 and 210 nm representing the heavy isotopomers are blue shifted to shorter wavelengths, relative to the parent curve $^{14}N^{14}N^{16}O$. At the same time the intensity of the absorption spectra around the peak between 177 and 183 nm for the $^{14}N^{14}N^{17}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O$, and $^{15}N^{15}N^{16}O$ isotopomers decrease. Nonetheless, the $^{15}N^{14}N^{16}O$ spectrum displays a small difference from the others in which the intensity around the peak is slightly increased. It should be noted that in the zero point energy model [10] the intensity of the absorption spectrum is not affected by the isotope substitution. The left shoulder, between 174 and 177 nm, of the absorption spectra of the heavy isotopomers are very slightly shifted. The agreement between the experimental and *ab initio* spectra are reasonably good at lower photon energy tail of the absorption spectra (between 195 and 210 nm) and demonstrates an excellent theoretical modeling of the N_2O photoabsorption process in the region of ultraviolet stratospheric window.

CONCLUSION

Rotational-vibrational energy levels for several important isotopomers of N_2O are variationally calculated for the ground electronic state, X^1A'. The agreement between the calculated vibrational energies and observed values for these isotopomers is shown to be good, especially for the three lowest excited vibrational states. The importance of the absorption spectra in modeling cometary atmospheres depends on both the magnitude of the spectra and the transition wavelength at which they peak. The absorption spectra reported here are in excellent agreement with the experimental observations and thus should reasonably be included in future isotopic modeling studies.

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Table 1. Comparison between calculated and experimental vibrational energies (cm^{-1}) for the X$^1A'$ ground state of $^{15}N^{14}N^{16}O$ isotopomer.

$v_1, v_2^{\|l\|}, v_3$	ΔE**(Theory)**^{a}	ΔE**(Experimental)**^{b}
$0, 0^0, 0$	0.00	0.00
$0, 1^1, 0$	579.88	585.31
$0, 2^0, 0$	1152.06	1159.97
$1, 0^0, 0$	1262.60	1269.89
$0, 3^1, 0$	1715.76	1736.65
$1, 1^1, 0$	1884.40	1862.77
$0, 4^0, 0$	2298.71	2305.16
$1, 2^0, 0$	2456.34	2439.62
$2, 0^0, 0$	2553.42	2534.53
$0, 5^1, 0$	2864.58	
$1, 3^1, 0$	3033.98	3020.10
$2, 1^1, 0$	3174.82	3135.58
$0, 6^0, 0$	3425.80	
$1, 4^0, 0$	3615.24	3589.93
$2, 2^0, 0$	3753.46	3712.13
$3, 0^0, 0$	3837.21	3795.45
$0, 8^0, 0$	4555.41	
$1, 6^0, 0$	4750.29	
$2, 4^0, 0$	4920.78	4866.89
$3, 2^0, 0$	5023.82	4976.65
$4, 0^0, 0$	5104.33	5054.91
$0, 10^0, 0$	5682.19	
$1, 8^0, 0$	5895.71	
$2, 6^0, 0$	6051.97	
$3, 4^0, 0$	6178.66	
$4, 2^0, 0$	6258.13	

[a] $\Delta E(\text{Theory}) = E(v_1, v_2, v_3) - E(0, 0^0, 0)$

[b] The experimental values were taken from references [15 - 17]

Table 2. Comparison between calculated and experimental vibrational energies (cm^{-1}) for the X$^1A'$ ground state of $^{14}N^{15}N^{16}O$ isotopomer.

$v_1, v_2^{\|l\|}, v_3$	ΔE**(Theory)**^{a}	ΔE**(Experimental)**^{b}
$0, 0^0, 0$	0.00	0.00
$0, 1^1, 0$	569.36	575.43
$0, 2^0, 0$	1141.75	1144.33
$1, 0^0, 0$	1251.83	1280.35
$0, 3^1, 0$	1697.71	
$1, 1^1, 0$	1860.49	1860.19
$0, 4^0, 0$	2275.58	2278.19
$1, 2^0, 0$	2440.13	2431.32
$2, 0^0, 0$	2530.84	2552.41
$0, 5^1, 0$	2835.89	
$1, 3^1, 0$	3006.19	3003.32
$2, 1^1, 0$	3139.84	3136.98
$0, 6^0, 0$	3391.16	
$1, 4^0, 0$	3583.08	3568.52
$2, 2^0, 0$	3726.38	3709.79
$3, 0^0, 0$	3810.02	3816.48
$0, 8^0, 0$	4509.34	
$1, 6^0, 0$	4704.81	
$2, 4^0, 0$	4881.63	
$3, 2^0, 0$	4986.10	4979.70
$4, 0^0, 0$	5072.39	5073.07
$0, 10^0, 0$	5629.79	
$1, 8^0, 0$	5836.20	
$2, 6^0, 0$	5998.39	
$3, 4^0, 0$	6131.89	
$4, 2^0, 0$	6218.33	

$^a\Delta E(\text{Theory}) = E(v_1, v_2, v_3) - E(0, 0^0, 0)$

^{b}The experimental values were taken from references [15 - 18]

Table 3. Comparison between calculated and experimental vibrational energies (cm^{-1}) for the X$^1A'$ ground state of ^{15}N^{15}N^{16}O isotopomer.

$v_1, v_2^{\lvert l \rvert}, v_3$	ΔE**(Theory)**^{a}	ΔE**(Experimental)**^{b}
$0, 0^0, 0$	0.00	0.00
$0, 1^1, 0$	565.45	571.89
$0, 2^0, 0$	1133.70	1136.45
$1, 0^0, 0$	1244.84	1265.33
$0, 3^1, 0$	1685.38	1702.00
$1, 1^1, 0$	1849.90	1842.41
$0, 4^0, 0$	2259.08	2261.47
$1, 2^0, 0$	2425.25	2409.46
$2, 0^0, 0$	2517.27	2523.25
$0, 5^1, 0$	2815.08	2822.14
$1, 3^1, 0$	2987.38	2977.74
$2, 1^1, 0$	3123.18	3105.94
$0, 6^0, 0$	3366.29	
$1, 4^0, 0$	3560.29	3538.48
$2, 2^0, 0$	3705.43	3674.71
$3, 0^0, 0$	3789.88	3774.24
$0, 8^0, 0$	4475.21	
$1, 6^0, 0$	4673.63	
$2, 4^0, 0$	4853.05	
$3, 2^0, 0$	4959.63	4932.00
$4, 0^0, 0$	5046.31	5019.08
$0, 10^0, 0$	5586.36	
$1, 8^0, 0$	5796.19	
$2, 6^0, 0$	5962.11	
$3, 4^0, 0$	6098.57	
$4, 2^0, 0$	6185.97	

[a] $\Delta E(\text{Theory}) = E(v_1, v_2, v_3) - E(0, 0^0, 0)$

[b] The experimental values were taken from references [17, 19]

Table 4. Comparison between calculated and experimental vibrational energies (cm^{-1}) for the X$^1A'$ ground state of $^{14}N^{14}N^{17}O$ isotopomer.

$v_1, v_2^{\|l\|}, v_3$	ΔE**(Theory)**[a]	ΔE**(Experimental)**[b]
$0, 0^0, 0$	0.00	0.00
$0, 1^1, 0$	580.98	586.36
$0, 2^0, 0$	1147.23	1161.55
$1, 0^0, 0$	1253.64	1264.70
$0, 3^1, 0$	1711.76	
$1, 1^1, 0$	1877.05	1858.76
$0, 4^0, 0$	2293.87	
$1, 2^0, 0$	2435.86	2435.73
$2, 0^0, 0$	2536.73	2524.67
$0, 5^1, 0$	2859.56	
$1, 3^1, 0$	3017.69	
$2, 1^1, 0$	3157.97	
$0, 6^0, 0$	3421.55	
$1, 4^0, 0$	3597.03	
$2, 2^0, 0$	3721.01	
$3, 0^0, 0$	3808.56	3781.65
$0, 8^0, 0$	4551.48	
$1, 6^0, 0$	4733.38	
$2, 4^0, 0$	4886.08	
$3, 2^0, 0$	4983.89	
$4, 0^0, 0$	5064.10	
$0, 10^0, 0$	5676.35	
$1, 8^0, 0$	5879.38	
$2, 6^0, 0$	6021.77	
$3, 4^0, 0$	6129.97	
$4, 2^0, 0$	6210.55	

[a] $\Delta E(\text{Theory}) = E(v_1, v_2, v_3) - E(0, 0^0, 0)$

[b] The experimental values were taken from references [15, 16]

Table 5. Comparison between calculated and experimental vibrational energies (cm^{-1}) for the X$^1A'$ ground state of $^{14}N^{14}N^{18}O$ isotopomer.

$v_1, v_2^{\|l\|}, v_3$	ΔE**(Theory)**[a]	ΔE**(Experimental)**[b]
$0, 0^0, 0$	0.00	0.00
$0, 1^1, 0$	578.62	584.23
$0, 2^0, 0$	1134.19	1155.14
$1, 0^0, 0$	1240.51	1246.88
$0, 3^1, 0$	1696.25	1729.35
$1, 1^1, 0$	1861.90	1839.94
$0, 4^0, 0$	2272.82	2294.02
$1, 2^0, 0$	2402.14	2411.51
$2, 0^0, 0$	2512.53	2491.19
$0, 5^1, 0$	2834.48	2861.63
$1, 3^1, 0$	2985.63	2990.18
$2, 1^1, 0$	3130.12	3093.36
$0, 6^0, 0$	3393.21	
$1, 4^0, 0$	3558.01	3555.68
$2, 2^0, 0$	3669.65	3661.02
$3, 0^0, 0$	3770.67	3735.37
$0, 8^0, 0$	4514.87	
$1, 6^0, 0$	4687.79	
$2, 4^0, 0$	4824.62	
$3, 2^0, 0$	4921.52	
$4, 0^0, 0$	5013.50	
$0, 10^0, 0$	5629.72	
$1, 8^0, 0$	5824.34	
$2, 6^0, 0$	5957.91	
$3, 4^0, 0$	6050.51	
$4, 2^0, 0$	6141.64	

[a] $\Delta E(\mathrm{Theory}) = E(v_1, v_2, v_3) - E(0, 0^0, 0)$

[b] The experimental values were taken from references [15 - 17]

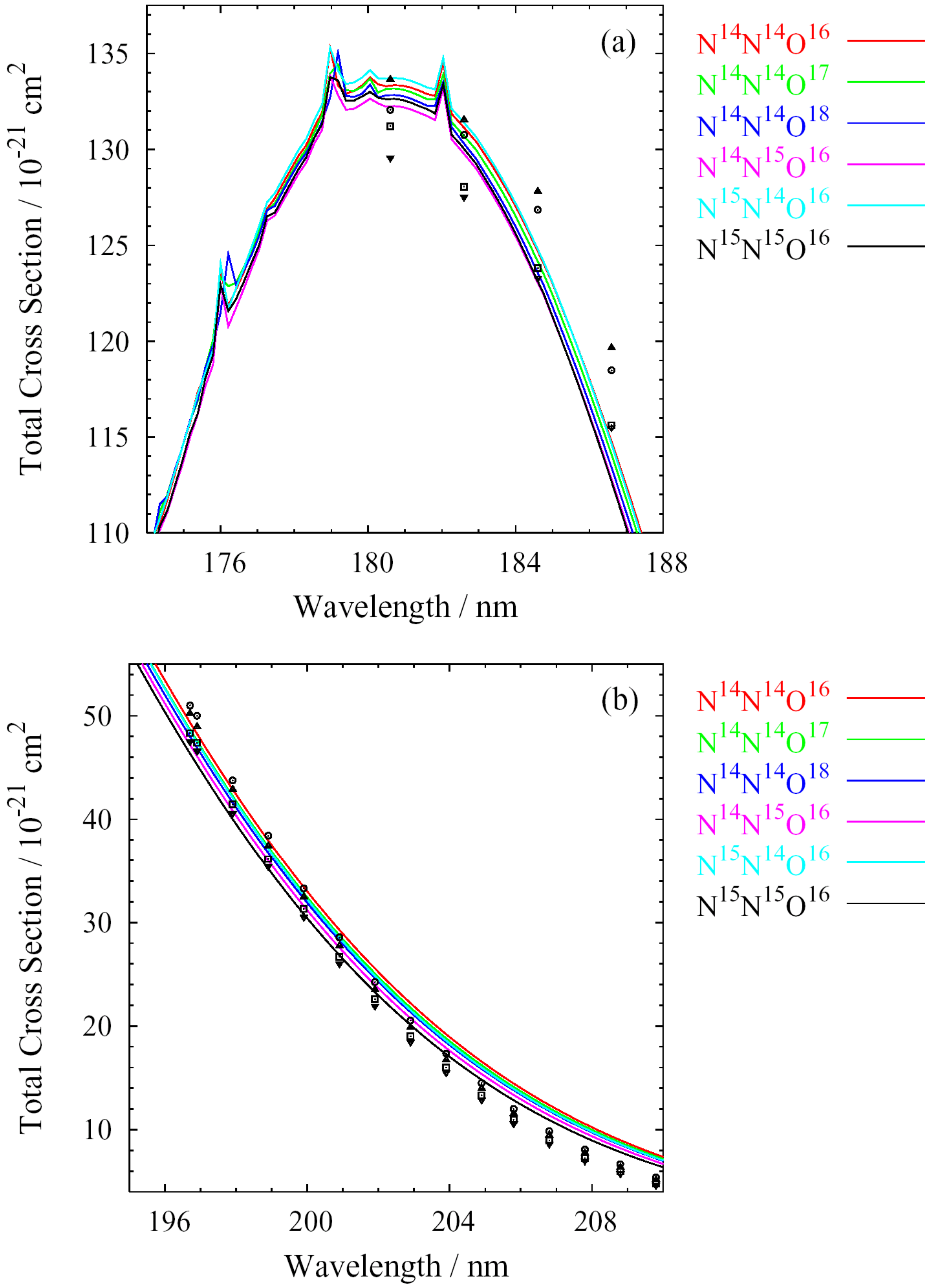

Figure 1. Comparison between the theoretical photoabsorption spectra at 233 K and the experimental spectrum of the N_2O molecule measured by von Hessberg et al. (233 K) [5]. Symbols ◯, □, △ and ▽ represent the experimentally measured spectrum of the $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{15}N^{15}N^{16}O$ isotopomers, respectively. (a) Region of the diffuse structure; (b) Region of the ultraviolet stratospheric window.