Infrared and microwave spectroscopy of ozone: historical aspects

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Abstract. The history of the development of infrared and microwave (vibrational-rotational) spectroscopy of ozone from the mid-19th century to the present is described. The development of both linear and nonlinear spectroscopy is discussed; to the extent that it is necessary, the neighbouring fields of the physics and chemistry of ozone (monitoring in the atmosphere, laser stimulation of chemical reactions, the study of relaxation processes, etc.) are also touched on. The current status of vibrational-rotational spectroscopy of ozone is assessed overall and the prospects for its future development discussed. A considerable body of reference information is provided.

1. Introduction

Ozone is an important constituent of atmospheric air, protecting man and all living things on the Earth against an excess of ultraviolet radiation. There has always been great interest in ozone and its role in physicochemical processes in the atmosphere, including global climate formation processes. Recently this interest has increased because of the threat of destruction of the ozone layer because of industrial emission of various gases and aerosols into the atmosphere, supersonic aviation flights, and other factors of a man-made character. Of the various methods for studying ozone optical methods in the infrared (IR) and microwave (MW) regions occupy a special place. This is because ozone has a number of strong vibrational–rotational absorption bands in the IR region of the

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Received 13 December 1993, in revised form 2 February 1994 Uspekhi Fizicheskikh Nauk 164 (7) 725-742 (1994) Translated by G J Bullen spectrum and also a strong rotational band in the microwave and far-IR region. In particular it is because of these bands that ozone plays an important part in the thermodynamics and optics of the atmosphere. The strong IR and MW absorption by ozone is used in various optical methods for monitoring the ozone content of the atmosphere. Finally, a detailed analysis of the vibrational-rotational and pure rotational spectra of the ozone molecule provides important information on its internal structure. The infrared spectroscopy of ozone has a history of more than 120 years. Over this period an extensive and



Figure 1. Growth in the number of publications on ozone physics since 1950 (the year when the heading 'ozone' made its appearance in *Physics Abstracts. Science Abstracts. Series A. Subject Index*): (1) ozone physics as a whole; (2) infrared and microwave spectroscopy of ozone. The data are taken from the above *Abstracts* for the period 1950-1991.

diverse body of experimental data has been accumulated, interpreted, and theoretically analysed. Development has taken place as it were by an avalanche-type mechanism embracing related scientific fields more and more, and generating new lines of investigation. This is clearly illustrated in Fig. 1, which shows a growth in the number of publications on the IR and MW spectroscopy of ozone and on the physics of ozone as a whole over the period from 1950 to 1991.

Apart from its educational aspect, which is of value to every researcher, dealing with the history of the spectroscopy of ozone also has a scientific-prognostic aspect. In the present review a retrospective analysis of the development of research on the vibrational-rotational (IR and MW) spectroscopy of ozone is presented, the current state of the subject is assessed, and an attempt is made to determine the immediate prospects for progress in this direction. The vibrational-rotational spectroscopy of ozone has always been closely connected with other fields of ozone physics and chemistry, and consequently a review of the spectroscopy of ozone must take into consideration these interrelationships. However, to give an equally detailed review of all the neighbouring fields is extremely difficult, at least within the scope of a journal. Hence in the present review we are forced to do no more than deal briefly with such fields as optical techniques for monitoring ozone in the atmosphere, the stimulation of chemical reactions of ozone by IR radiation, composite optical methods for studying ozone, etc. To compensate for this lack of completeness we have tried to give detailed references where possible. To make reading of the material easier the text of the historical review is preceded by a section in which concise data on the structure of the ozone molecule and its vibrational-rotational spectra are given.

2. Concise data on the structure of the O_3 molecule and its vibrational – rotational spectra

The triatomic ozone molecule has a bent structure. The majority of its isotopic modifications are symmetric, e.g. ${}^{16}O_{32}$, ${}^{18}O_{3}$, and ${}^{17}O_{3}$. In other instances (${}^{16}O^{16}O^{18}O$, $^{18}O^{18}O^{16}O$, etc.) the configuration of the molecule is asymmetric. In the principal modification of ozone ${}^{16}O_3$, which is the most abundant under natural conditions (99.28%), the atoms are situated at the corners of an obtuse-angled isosceles triangle with an angle of 116° 47' between sides of length 1.2717 Å (Fig. 2). The ozone molecule has three nondegenerate normal vibrations which are active both in the absorption and in the Raman spectra. The vibrational spectrum of ozone is described by three quantum numbers v_1 , v_2 , and v_3 (or v_1 , v_2 , and v_3) which characterise the degree of excitation of the symmetric stretching (v_1) , bending (v_2) , and asymmetric stretching (v_3) types of normal vibration, respectively. The strongest transitions are those obeying the selection rules for a harmonic oscillator $\Delta v_i = \pm 1$ (i = 1, 2, 3), and an overtone and combination band spectrum appears only due to anharmonicity of the vibrations. The centres of the most intense IR absorption bands of ${}^{16}O_3$ are as follows: v_3 1042.08 cm⁻¹ (9.6 µm), $v_1 + v_3$ 2110.79 cm⁻¹ (4.74 µm), v_2 700.93 cm⁻¹ (14.27 µm), v_1 1103.14 cm⁻¹ (9.07 µm), and $v_2 + v_3 - v_2$ 1025.60 cm⁻¹ (9.75 µm). The intensities of these bands are in the ratios 1:0.084:0.047: 0.039:0.033. The geometrical parameters of the ozone molecule change



Figure 2. Equilibrium geometry of the ${}^{16}O_3$ molecule in the electronic ground state [72] and its normal vibrations. The axes *a*, *b*, and *c* correspond to the principal axes of the inertia tensor of the molecule.

Table 1. Mean geometrical parameters of the ${}^{16}O_3$ molecule in different vibrational states [72].

Vibrational state	r/Å	θ	
(000)	1.2792	116° 46′	
(100)	1.2844	116° 37″	
(010)	1.2807	117° 04″	
(001)	1.2875	116° 37″	
(020)	1.2821	117° 22′	

on vibrational (Table 1) and electronic excitation and are also different for different isotopic modifications.

Ozone has a fairly large permanent dipole moment (0.53 D) and consequently a fairly intense rotational absorption band in the far-IR, submillimetre, and millimetre wavelength ranges ($\lambda \approx 0.05 - 20$ mm). The ozone molecule is a slightly asymmetric prolate top. To describe its rotational spectrum three quantum numbers are used: J for the total angular momentum, and K_a and K_c for the projections of the total angular momentum onto the axes of the minimum (axis a) and maximum (axis c) moments of inertia, respectively. The quantum numbers K_a and K_c can take the values $0 < K_a$, $K_c < J$. The transition in the IR spectrum permitted by the selection rules are $\Delta J = -1, 0,$ and +1, corresponding to the P-, Q-, and R-branches of a vibrational-rotational band (Fig. 3). The numbers K_a and K_c do not obey such rigid selection rules but their changes depend on the type of band. For example, for a pure rotational band and the vibrational-rotational bands v_1 and v_2 of symmetric configurations ΔK_a , $\Delta K_c = \pm 1, \pm 3$, and for the band v_3 of symmetric configurations $\Delta K_a = 0$, $\pm 2, \pm 4, \dots$ and $\Delta K_c = \pm 1, \pm 3, \dots$. For the ¹⁶O₃ molecule the most intense transitions are ΔK_a , $\Delta K_c = 0, \pm 1$. The probability value for transitions with $|\Delta K_a, \Delta K_c| > 1$ depends on the degree of asymmetry of the inertia tensor of the molecule, which is described by the asymmetry parameter $\kappa = (2B - A - C)/(A - C)$, where A, B, and C are rotational constants that are inversely proportional to the moments of inertia along the principal axes. For the ground vibrational state of the ${}^{16}O_3$ molecule $A = 3.551 \text{ cm}^{-1}$, $B = 0.445 \text{ cm}^{-1}$, $C = 0.349 \text{ cm}^{-1}$, and $\kappa = -0.968$. Since for ozone $|\kappa| \approx 1$, the probabilities of the transitions with $|\Delta K_a, \Delta K_c| > 1$ in its rotational spectra are extremely low (Fig. 4). Note that, for molecules of the symmetric top type, $|\kappa| = 1$ and such transitions are forbidden. The spectra of the ozone molecule have a



Figure 3. Rotational structure of the (001) - (000) band ($\lambda \approx 9.6 \ \mu\text{m}$) of the ${}^{16}\text{O}_3$ molecule according to data taken from the tables of Barbe et al. [56]. The numbers on the curves indicate the quantum number K_a in a series of vibrational-rotational lines with the same

00)-(¹⁰⁰)A/(A) $\langle \rho \rangle / (\mathrm{cm}^{-1})^{-1}$ 10^{-2} 60 50 $= \pm 2$ 40 10^{-6} 30 20 10^{-8} 10 = +2 ± 4 10^{-10} 0 1000 1020 1040 1060 1080 1100 1120 v/cm

Figure 4. Frequency dependence of the mean spectral density (full lines) and mean probability (broken lines) for allowed ($\Delta K_a = 0$) and unfavoured ($\Delta K_a = \pm 2, \pm 4$) vibrational-rotational transitions in the (001)-(000) band of ${}^{16}O_3$; by calculation [216], averaging range 2 cm⁻¹.

complex and irregular rotational structure and there are no simple formulas for calculating them.

The infrared spectra of ozone are considerably complicated by Darling–Dennison anharmonic resonance interactions and Coriolis vibration–rotation interactions. These interactions manifest themselves as changes in the rotational

quantum number J. The lower part of the figure shows the experimental values of the absorption coefficients of an ozone-air mixture for the lines in the 9P branch of CO_2 -laser radiation [128].

constants of coupled vibrational states and as anomalies in the positions and intensities of certain lines. In the O₃ molecule the Coriolis interaction couples the states (v_1, v_2, v_3) and $(v_1 \mp 1, v_2, v_3 \pm 1)$, $(v_1, v_2 \pm 2, v_3 \mp 1)$; and the Darling–Dennison interaction couples the states (v_1, v_2, v_3) and $(v_1 \mp 2, v_2, v_3 \pm 2)$. The lower levels for O₃ which are coupled by these interactions are shown in Fig. 5.



Figure 5. Lower vibrational levels of the electronic ground state of the ${}^{16}O_3$ molecule. The wavy lines indicate the Darling–Dennison anharmonic resonance interactions and the dotted lines the Coriolis vibration–rotation interactions.

3. The history of the development of the vibrational – rotational spectroscopy of ozone

3.1 Linear spectroscopy

The infrared spectroscopy of ozone has a long history. As early as 1872 the English physicist John Tyndall observed strong absorption of thermal radiation by ozone [1]. In 1904 the Swedish geophysicist-spectroscopist Knut Johan Ångstrom measured the absorption spectrum of ozone in the IR region for the first time [2, 3]. However, as the ozone concentration in his experiments was low he found only the four strongest bands with the following wavelengths: 4.8 µm (band with a sharp spectral profile), 5.8 µm (weak band), 6.7 µm (which may not belong to ozone), and 9.6-10 µm (very strong, possibly a double band). Studies of the IR spectrum using higher ozone concentrations and a more refined method for its preparation were carried out by Ladenburg and Lehmann in 1906 [4]. They found four more bands—at 1.1, 3.7, 7.6, and 11.35 µm — which, as was shown subsequently, also do not all belong to ozone.

At the early stages of the study of the spectra of ozone there were considerable difficulties in obtaining chemically pure O₃ and hence incorrect interpretations of the spectrum and false conclusions regarding the molecular structure. In particular, for a long time the N₂O₅ bands at 11.35 and 7.6 µm (which had been found by Ladenburg and Lehmann) were thought to belong to O_3 . Furthermore, one of these bands (at 7.6 µm) was interpreted as the fundamental band v_1 of O₃ [5]. Eliminating the N₂O₅ bands at 5.9 µm [6, 7], 11.35 µm [5], and 7.6 µm [8] was an important step in the development of the IR spectroscopy of ozone. At that time ozone was normally produced with the aid of a standard Siemens' ozonizer, which gives only up to 10% ozone, and it was not until 1930 that a better method using a glow discharge in oxygen with the tube cooled with liquid air [9] was proposed. This new method [9], which enabled almost pure ozone to be obtained, was used as long ago as 1932 by Gerhard [5].

In 1934 a pure ozone spectrum which was of very high quality for that time, covering a broad range of wavelengths $(1-27 \mu m)$ and containing 6 bands, was obtained by Hettner, Pohlman, and Schumacher [8]. These results were regarded as standard right up to 1948. However numerous attempts to interpret the spectrum of O_3 , including those using the data of Hettner et al. [8], gave inconsistent results. At that time there was still no single view as to the structure of the O₃ molecule and the experimental data were interpreted both with acute-angled and with obtuse-angled molecular models. In the 1930s and 1940s there was much discussion on this question [5, 8, 10-17]. The supporters of the acute-angled model regarded even the results of direct measurements of the geometrical parameters of O3 made by electron diffraction in 1941 [14], as unconvincing. An incorrect interpretation of the IR spectrum of ozone based on the results of Hettner, Pohlman, and Schumacher is also contained in Herzberg's classic monograph published in English in 1945 and translated into Russian in 1949 [18].

It was not until 1948 that a correct interpretation of most of the known IR bands of ozone was given by Wilson and Badger [19] on the basis of their own more accurate measurements of the relative band intensities. They also discovered a very weak O_3 band in the 9 µm region, which

they interpreted as v_1 . This settled the outcome of many years' discussion on the interpretation of the ozone spectrum and the true structure of the molecule in favour of the obtuse-angled model. Wilson and Badger's interpretation [19] of the band centres is: 705 cm⁻¹ v_2 , 1043 cm⁻¹ v_3 , 1110 cm⁻¹ v_1 , 1740 cm⁻¹ $v_2 + v_3$, 2105 cm⁻¹ $v_1 + v_3$, etc. With these results the force constants and thermodynamic characteristics of ozone were calculated correctly for the first time [20, 21] and the acute-angled model of the molecule was subjected to strong criticism [22].

Improvement of classical spectrometers enabled the absorption spectrum of O₃ to be measured more accurately and made it possible to record and identify previously unknown weak bands. In 1968 McCaa and Shaw [23] measured the positions of (band) centres to within ± 2 cm⁻¹ and identified 14 vibrational-rotational bands of O_3 in the range 600-3200 cm⁻¹. A complete set of anharmonic constants x_{ij} was also determined for the first time. The next major advance in the IR spectroscopy of ozone was the publication in 1974 of work [24] in which the centres of 18 ${}^{16}O_3$ bands and 15 ${}^{18}O_3$ bands were measured to within ± 1 cm⁻¹. Information on isotopic bands of ozone was obtained for the first time. The experimental data of Barbe et al. [24] enabled the energies of 21 vibrational states of ${}^{16}O_3$ and 18 states of ${}^{18}O_3$ to be calculated. In 1982 Imre et al. [25] used the resonance fluorescence method to determine the positions of another 8 highly placed levels of ozone, no information on which had been given by Barbe et al. [24]. Although the accuracy of measurement of the band centres was low $(\pm 10 \text{ cm}^{-1})$, energy levels up to 7495.6 cm⁻¹ [the (700) state] were obtained. More accurate values $(\pm 3 \text{ cm}^{-1})$ of the energies of nine vibrational states with $v_2 = 0$ and the sum of the vibrational quantum numbers $v_1 + v_3 \leq 5$ were later obtained by Rawlins and Armstrong [26] from the IR chemiluminescence spectra of O_3 accompanying the recombination reaction $O + O_2 +$ $M \rightarrow O_3 + M$ [27]. In 1990 Adler-Golden et al. [28, 29] measured the centres of 17 chemiluminescence bands of O_3 in the upper atmosphere to an accuracy of $\pm (2-4)$ cm⁻¹ and determined the positions of the levels with $v_1 + v_2 + v_3 \leq 7$ and $v_2 = 0.1$. The maximum energy of the observed vibrational states was 6353 cm^{-1} [(115) state]. The current interest in studying highly placed vibrational

Table 2. Vibrational levels of the ${}^{16}O_3$ molecule (cm⁻¹) [24, 25, 28, 106, 108, 110–113, 116].

$(v_1v_2v_3)$	E_v	$(v_1v_2v_3)$	E_{v}	$(v_1v_2v_3)$	E_v
(010)	700.9311	(003)	3046.0882	(311)	4894
(001)	1042.0840	(102)	3083.7024	(005)	4919
(100)	1103.1373	(201)	3186.4097	(104)	4926
(020)	1399.2726	(300)	3289	(302)	5145
(011)	1726.5225	(121)	3457.5	(500)	5435
(110)	1796.2619	(013)	3698.2942	(015)	5517
(002)	2057.8908	(112)	3743	(114)	5536
(030)	2095.02	(211)	3849.4	(006)	5771
(101)	2110.7843	(004)	4000	(105)	5778
(200)	2201.1552	(103)	4020	(402)	6187
(021)	2407.9345	(202)	4136	(016)	6345
(120)	2486.5766	(301)	4252	(115)	6353
(012)	2726.1066	(400)	4357	(600)	6497
(111)	2785.2391	(014)	4633	(602)	7207
(210)	2886.1781	(113)	4660	(700)	7523

Table 3. Vibrational levels of isotopic modifications of the ozone molecule (cm^{-1}) [24, 103, 104, 109, 115].

$(v_1v_2v_3)$	¹⁸ O ₃	¹⁶ O ¹⁶ O ¹⁸ O	¹⁸ O ¹⁶ O ¹⁸ O	¹⁸ O ¹⁸ O ¹⁶ O	¹⁶ O ¹⁸ O ¹⁶ O
(010)	661.4925	684.6134	668.0850	677.5038	693.3057
(001)	984.6	1028.1120	1019.1	_	1008.4528
(100)	1041.9	1090.3541	_	_	1074.3076
(020)	-	-	-	-	-
(011)	1631.2	1695.4	1671.2	1656.8	_
(110)	1695.9	-	-	-	-
(002)	1945.4	_	_	_	_
(030)	-	_	_	_	_
(101)	1995.1	2090.0	2060.1	2027.5	2049.3
(200)	2079.4	_	_	_	_
(021)	-	_	_	_	_
(120)	_	_	_	_	_
(012)	2579.5	_	_	-	-
(111)	2634.3	2748.5	2703.4	2680.5	2718.1
(210)	_	_	_	_	_
(003)	2883.2	2998.8	2980.3	2903.0	_
(102)	_	_	_	_	_
(201)	3012.6	-	-	-	-
(300)	-	_	_	_	_
(121)	3271.0	_	_	_	_
(013)	3501.4	-	-	-	-
(112)	_	_	_	_	-
(211)	-	-	-	-	-
(004)	_	_	_	_	_
(103)	3814.1	-	-	-	-

states of the asymmetric mode of ozone is to a considerable extent due to the important contribution that they make to the inherent radiation of the Earth's upper atmosphere which arises from three-body recombination of O_3 [30]. Current data on the vibrational levels of ozone are given in Tables 2 and 3.

The strongest band in the IR spectrum of ozone is $v_3 (\lambda = 9.6 \,\mu\text{m})$. Ångstrom noted that this band must contribute greatly to absorption of IR radiation in the Earth's atmosphere and must therefore play an important role in its radiation balance [2, 3]. The study of the 9.6 μm band of O₃ under both laboratory conditions and in the atmosphere received considerable attention from the beginning of the century [2–4, 8, 31–39]. The integrated absorption of this band has been studied by Strong [37–39], Vigroux [40], Paetzold [41], and Raschke [42]. The most detailed experimental results were obtained by Walshaw [43–45] and Gal'tsev [46].

The strong absorption of radiation in the 9.6 μ m O₃ band provided a basis for developing new methods for remote measurement of the ozone content of the atmosphere. For example, in 1941 Strong showed that the absorption in the 9.6 μ m band is markedly dependent on the air pressure and he suggested using this property to find the height of the ozone layer in the atmosphere [39]. From the end of the 19th century optical studies of atmospheric ozone were normally carried out in the UV and visible regions of the spectrum (in the Hartley and Chappuis bands) but as long ago as the late 1930s measurements in the IR region began to be used for these purposes [37, 47]. Subsequently IR spectra were used to determine the mean temperature of the ozone layer [48] and to investigate seasonal variations in the absorption of solar IR radiation by atmospheric ozone [49]. In 1952-1954 in Cambridge, England Goody and Walshaw carried out detailed experiments to determine the height of the centre of the ozone layer in the atmosphere by investigating the absorption of solar radiation in the $9.112-9.814 \mu m$ range [50]. An annotated bibliography of papers on ozone in the atmosphere (including optical methods of investigations) in the period 1858-1953 has been published [51]. Khrgian's book [52] also contains much valuable information.

Further progress in investigating the 9.6 μ m band of O₃ resulted from the development of high-resolution spectroscopy, which made it possible to study its rotational structure (see Fig. 3). The rotational structure of O_3 IR bands had been partially resolved by Gerhard as long ago as 1932 [5]. He found that the ozone bands have a structure resembling that of an asymmetric spinning top and concluded that the molecule has a nonlinear shape. The first studies of the 9.6 and 14.2 µm bands at higher resolution were carried out by Adel et al. in 1936 [13] (investigating the 9.6 µm spectrum of solar radiation passing through the atmosphere) and by Adel and Dennison in 1946 [16] (laboratory studies of the 14.2 µm band). The results obtained were of a preliminary nature as they were neither accurate nor complete. Systematic studies of the rotational structure of O_3 bands were started in 1952 by Migeotte et al. [53], who measured the spectrum of the 9.6 μ m band over the range 989-1070 cm⁻¹ to an accuracy of $\pm 0.1 \text{ cm}^{-1}$ and gave empirical formulas for calculating the centres of the vibrational-rotational lines. These results were later refined and augmented [54, 55] but the 9.6 µm band was not fully investigated until 1977 [56]. Ref. [56] includes extensive tables of parameters of the vibrationalrotational lines of the v_3 band of O_3 . The centres of the lines were measured to an accuracy of 30-100 MHz (0.001 - 0.003 cm^{-1}). Systematic studies of the structure of other ozone bands had also been started by Vigroux et al. in 1953 [57]. More detailed analyses of the ozone bands v_2 , $v_1 + v_3$, v_1 , and $v_1 + v_2 + v_3$ were published later in Refs [58], [59, 60], [55], and [61], respectively.

In the second half of the 1940s experimental techniques improved dramatically because of the increase in general technological and industrial potential during World War II. Ultrahigh-frequency technology, which was used in radiolocation systems, was developed in particular. Because of this the new field of *microwave spectroscopy* developed rapidly in the post-war years. Up to this time molecular structure was usually investigated with the use of IR spectroscopic methods. However, the different frequency range, high resolving power, and precision of microwave spectrometers made it possible to investigate phenomena of quite a different class: Stark and Zeeman effects, hyperfine splitting, collision-induced line broadening, etc. [62].

A detailed study of the structure of the pure rotational bands of O_3 occurring in the microwave region started in 1953. The first measurements of the microwave spectrum of ozone were made by Trambarulo et al. [63] and Hughes [64]. The former [63] obtained the spectrum in the range 42–118 GHz and determined the geometrical param- eters, dipole moment, and molecular *g*-factor of the ¹⁶O₃ molecule. The value found for the dipole moment (0.53 D) is considerably more precise than the first result (0.49 D) obtained in 1939 by Lewis and Smyth [65] and is almost the same as that found by Epprecht in 1950

Parameter		Value	
Electric dipole moment	μ	0.5337 D	
Electric polarisability anisotropy:	$\alpha_{aa} - \bar{\alpha}$	2.04 Å [3]	
	$\alpha_{bb} - \bar{\alpha}$	-0.98 Å [3]	
	$\alpha_{cc} - \overline{\alpha}$	-1.03 Å [3]	
Rotational g-factors along the principal axes:	g_{aa}	$-2.9877 \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
	g_{bb}	$-0.2295 \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
	g_{cc}	$-0.0760 \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
Mean magnetic susceptibility	$\bar{\chi}$	$8.00 \times 10^{-6} \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
Magnetic susceptibility anisotropy:	$\chi_{aa} - \bar{\chi}$	$23.85 \times 10^{-6} \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
	$\chi_{bb} - \bar{\chi}$	$0.41 \times 10^{-6} \text{ erg } \text{G}^{-2} \text{ mol}^{-1}$	
	$\chi_{cc} - \bar{\chi}$	$-24.20 \times 10^{-6} \text{ Erg G}^{-2} \text{ mole}^{-1}$	
Electric quadrupole moments about principal axes	$ heta_{aa}$	-1.37×10^{-26} esu cm ²	
	$ heta_{bb}$	-0.80×10^{-26} esu cm ²	
	$ heta_{cc}$	2.17×10^{-26} esu cm ²	

Table 4. Electric and magnetic parameters of the ¹⁶O₃ molecule in different vibrational states [72].

(0.52 D) [66]. The first data on the rotational constants of isotopic modifications of ozone were obtained by Hughes in 1956 [67]. Subsequent studies of the microwave and far-IR spectra of ozone provided more accurate determinations of the rotational constants and geometrical parameters of the O₃ molecules, and also their electric and magnetic constants [68–79] (Table 4). The magnetic parameters of the O₃ molecule were measured [69, 75] with the use of the Zeeman effect, and electric and magnetic constants of O₃ were determined with the combined Stark–Zeeman effect [76, 77]. A detailed review and analysis of the microwave spectrum of ozone based on data published up to 1978 has been given by Lovas [79].

One other point has to be noted in relation to the rapid progress in microwave spectroscopy in the post-war years. The development of high-resolution spectroscopy, as with any other field of science, has always depended to a considerable extent on the development of theory. Although molecule quantum mechanics made considerable progress in the 1920s-1940s a number of its areas were not devel-oped sufficiently at that time. One such area was the theory of the spectra of nonrigid asymmetric tops. Because of the lack of good computer techniques data on the energy levels of actual (nonrigid) molecules with arbitrary values of the rotational quantum number J could not be obtained. For a long time, analyses of the spectra of asymmetric tops were carried out with King, Hainer, and Cross's tables, which contain data for calculating energy levels of rigid tops with J < 11 [80] and the intensities of lines with J > 12 [81]. It was not until 1952 that Kivelson and Wilson [82] proposed a method for analysing the spectra while allowing for the effect of nonrigidity. One can say that the theory 'matured' just at the time when systematic experimental studies of the rotational structure of the ozone bands were being started. Analysis of the vibrational-rotational spectra of ozone was performed successfully with the Kivelson-Wilson formalism up to the early 1970s. A more general approach, including a proper description of the rotation of nonplanar molecules, was developed by Watson in the late 1960s [83-86]. Watson's formalism of effective Hamiltonians is currently the main method for analysing the rotational structure of molecular spectra, including the spectra of ozone. Full use of this method was possible only with the advent of computers.

The major enhancement of the potentialities of highresolution spectroscopy resulting from the development of laser technology, Fourier spectroscopy, and computer facilities gave a new impetus to research on the rotational and vibrational-rotational spectra of O_3 . Spectral resolutions of 0.001 cm⁻¹ became common practice and the resolution of microwave spectrometers reached 0.1 MHz. The development of spectroscopy at this time was to a considerable extent due to practical demands: laser location and communications, remote probing of the atmosphere, Earth-space radio communications, etc. There was an urgent necessity to predict the results of passing narrowband laser radiation through the atmosphere and to interpret the relevant experiments.

As early as the late 1960s and early 1970s a sufficient level of knowledge of the rotational spectra of O₃ had been achieved for the ozone content of the atmosphere to be determined by making the appropriate measurements in the microwave region of the spectrum [87–89]. For example, Caton et al. [87] made measurements of the solar radiation spectrum using a millimetre radiometer ($\lambda \approx 8$ mm), and Harries and Burroughs [89] recorded spectra of stratosphere radiation in the submillimetre range ($\lambda \approx 0.15-0.50$ mm) using a Fourier spectrometer. Considerable attention was paid to obtaining precise values of coefficients of absorption



Figure 6. Spectrum of the absorption coefficient of ozone in the microwave region ($\lambda \approx 0.3-100$ mm). The calculation was made [90] for typical conditions at sea level ($N_{O_3} = 10^{11}$ cm⁻³, P = 1 atm, T = 200 K) with the use of Gora's data [70].

Table 5. Microwave absorption coefficients of O₃ ($\lambda \approx 1.5-20.2 \text{ mm}$) at the centres of some rotational lines (calculation [91] with a Lorentz profile for $\gamma = 4.6 \text{ MHz Torr}^{-1}$ and T = 30 K).

Transition		Frequency/GHz	Absorption	
J', K'_a, K'_c	$J^{\prime\prime},K_a^{\prime\prime},K_c^{\prime\prime}$		7	
23, 4, 20	24, 3, 21	14.8665	2.9×10^{-6}	
18, 3, 15	19, 2, 18	23.8595	9.0×10^{-6}	
15, 3, 13	16, 2, 14	30.0517	1.7×10^{-5}	
18, 2, 16	17, 3, 15	37.8324	2.8×10^{-5}	
12, 2, 10	13, 1, 13	43.6531	2.3×10^{-5}	
7, 2, 6	8,1,7	53.6881	4.5×10^{-5}	
16, 3, 13	17, 2, 16	61.9267	6.5×10^{-5}	
6, 0, 6	5, 1, 5	67.3562	1.5×10^{-4}	
12, 1, 11	11, 2, 10	76.5337	1.5×10^{-4}	
2, 1, 1	2, 0, 2	96.2284	2.8×10^{-4}	
4, 1, 3	4, 0, 4	101.7367	5.4×10^{-4}	
6, 1, 5	6, 0, 6	110.8359	8.4×10^{-4}	
8, 1, 7	8, 0, 8	124.0873	1.2×10^{-3}	
19, 4, 16	20, 3, 17	136.8602	2.8×10^{-4}	
14, 1, 13	13, 2, 12	144.9194	6.3×10^{-4}	
12, 1, 11	12, 0, 12	165.7844	2.2×10^{-3}	
18, 4, 14	19, 3, 17	175.4458	4.7×10^{-4}	
10, 0, 10	9, 1, 9	184.3778	2.0×10^{-3}	
14, 1, 13	14, 0, 14	195.4302	2.8×10^{-3}	

of radiowaves by the various gaseous constituents in the atmosphere [90, 91]. Data on the absorption coefficients of ozone in the microwave region of the spectrum are given in Fig. 6 and Table 5.

In the last 10-15 years considerable progress has been achieved in the high-resolution spectroscopy of ozone; previous results have been revised and many new results obtained (Table 6). For example, El-Sherbihy el al. [92] used a tunable diode laser to measure the frequencies of the centres of more than 100 lines in the v_3 band of O_3 to within only 3-10 MHz, which is ten times more accurate than the data in the tables of Barbe et al. [56]. An IR laser heterodyne technique has been used to obtain spectra of ozone in the laboratory and in the atmosphere with a resolution of 5 MHz [93]. The use of Fourier spectrometers in studies of the fundamental bands of O_3 gave somewhat lower accuracy (0.001 cm⁻¹ on average). However, in recent vears measurements of the rotational spectra of ozone in the far-IR by means of tunable Fourier spectrometers have reached an accuracy of 0.05 MHz [94].

By the use of modern methods inverse problems have been solved with a large body of experimental data: new values have been obtained and previous values refined for the molecular and spectroscopic constants of ozone [95 – 121, 253, 254], including its isotopic modifications [103 – 105, 109, 115, 119 – 121, 254], and also electro-optical [122 – 124] and potential [125, 126, 254] constants (Tables 7 – 12). Considerable attention has been paid to experimental studies of

Table 6. Infrared absorption bands of the ozone molecule that have been studied at high resolution.

Band	Isotope code ^a	Band centre/cm ⁻¹	Range/cm ⁻¹	Number of lines	Sum of intensi- ties/cm per molecule	Accuracy of line position/cm ⁻¹	Accuracy of line intensity (%)	R ef.
(000) - (000)	666	_	0-191	3982	4.387×10^{-19}	_	_	[139]
(010) - (000)	888	661.4925	-	-	5.930×10^{-19}	0.0053	_	[115]
(010) - (000)	868	668.0850	_	_	6.020×10^{-19}	0.0077	_	[115]
(010) - (000)	688	677.5038	-	-	6.000×10^{-19}	0.0074	_	[115]
(010) - (000)	668	684.6134	-	-	6.490×10^{-19}	_	_	[109]
(010) - (000)	667	692.4347	_	_	5.180×10^{-19}	0.0078	_	[117]
(010) - (000)	686	693.3057	_	-	6.450×10^{-19}	_	_	[109]
(010) - (000)	676	697.0793	_	_	5.650×10^{-19}	0.0083	_	[117]
(020) – (010)	666	698.3443	573 - 865	4591	4.164×10^{-20}	0.0006	5	[139]
(010) – (000)	666	700.9314	560 - 895	6340	6.283×10^{-19}	0.0006	5	[139]
(012) – (110)	666	929.8447	940 - 1010	164	3.290×10^{-23}	_	_	[119]
(002) – (100)	666	954.7535	920 - 1050	951	3.270×10^{-21}	-	_	[119]
(001) – (000)	888	984.8188	925 - 1150	_	_	0.001	_	[105]
(111)-(110)	666	988.9772	930 - 1020	1342	2.100×10^{-21}	-	_	[119]
(012) – (011)	666	999.5841	935 - 1035	1603	6.000×10^{-21}	-	_	[119]
(101) – (100)	666	1007.6470	920 - 1170	2646	6.252×10^{-20}	_	_	[119, 139]
(001) - (000)	686	1008.4528	935 - 1070	2095	1.325×10^{-17}	-	_	[119, 139]
(021) - (020)	666	1008.6618	950 - 1060	1511	1.500×10^{-20}	_	_	[119]
(002) – (001)	666	1015.8068	935 - 1150	3137	1.680×10^{-19}	-	_	[119, 139]
(001) – (000)	868	1019.3499	925 - 1150	_	_	0.001	_	[105]
(011) – (010)	666	1025.5914	935 - 1220	3883	4.640×10^{-19}	_	_	[119]
(001) - (000)	668	1028.1120	955 - 1130	3827	1.280×10^{-17}	-	_	[119]
(100) - (000)	888	1041.5556	925 - 1150	-	_	0.001	_	[105]
(001) - (000)	666	1042.0840	919 - 1244	7224	1.410×10^{-17}	0.0006	10	[119, 139]
(111) – (011)	666	1058.7166	950 - 1090	252	6.380×10^{-23}	_	_	[119]
(101)-(001)	666	1068.7003	940 - 1180	2558	5.240×10^{-21}	-	_	[119]
(100) – (000)	868	1072.2172	925 - 1150	-	-	0.001	_	[105]
(100) - (000)	686	1074.3076	970 - 1140	888	2.270×10^{-19}	0.001	_	[105, 119]
(120) – (020)	666	1087.3041	1035 - 1170	820	2.210×10^{-22}	_	_	[119]

Table 6. (continued)

Band	Isotope code ^a	Band centre/cm ⁻¹	Range/cm ⁻¹	Number of lines	Sum of intensi- ties/cm per molecule	Accuracy of line position/cm ⁻¹	Accuracy of line intensity (%)	Ref.
(210) – (110)	666	1089.9162	1090 - 1160	177	3.330×10^{-23}	_	_	[119]
(100) – (000)	668	1090.3541	970 - 1150	4425	1.124×10^{-18}	0.001	10	[109, 119]
(110) – (010)	666	1095.3308	950 - 1235	3885	1.270×10^{-20}	-	-	[119, 139]
(200) – (100)	666	1098.0179	950 - 1215	2931	3.300×10^{-21}	_	_	[119]
(100) – (000)	666	1103.1373	942 - 1271	6766	5.400×10^{-19}	0.0006	10	[119, 139]
(200) – (001)	666	1159.0712	970 - 1230	2057	8.340×10^{-21}	_	_	[119]
(210)-(011)	666	1159.6556	1135 - 1200	593	1.650×10^{-22}	_	_	[119]
(101) – (010)	666	1309.8532	_	-	1.010×10^{-21}	_	_	[110]
(020) - (000)	666	1399.2726	_	_	5.430×10^{-22}	_	_	[110]
(021) – (010)	666	1707.0034	1650 - 1730	1365	3.420×10^{-21}	0.002	20	[112, 113]
(011) – (000)	666	1726.5277	1657 - 1910	1709	5.373×10^{-20}	0.0043	10	[139]
(120) - (010)	666	1785.6456	1720 - 1875	1621	1.370×10^{-21}	0.002	20	[112, 113]
(110) - (000)	666	1796.2606	1681 - 1927	2137	2.266×10^{-20}	0.0043	10	[139]
(003) - (100)	666	1942.9509	1860 - 2100	1285	1.380×10^{-21}	_	_	[113]
(102) – (100)	666	1980.5651	1875 - 2070	1245	3.840×10^{-22}	_	_	[113]
(003)-(001)	666	2004.0042	1890 - 2080	1685	1.190×10^{-21}	_	_	[113]
(012) – (010)	666	2025.1755	1910 - 2120	2506	3.160×10^{-21}	_	_	[113]
(102)-(001)	666	2041.6184	1970 - 2070	2175	1.560×10^{-20}	_	_	[113]
(002) - (000)	666	2057.892	1945 - 2140	2164	1.107×10^{-19}	0.0047	8–30	[139]
(201) – (100)	666	2083.2724	2000 - 2130	1976	1.050×10^{-20}	_	_	[113]
(111)-(010)	666	2084.3132	2029 - 2107	1469	3.743×10^{-20}	0.004	10-30	[139]
(101) – (000)	666	2110.785	1968-2164	2165	1.134×10^{-18}	0.0047	8–30	[139]
(201)-(001)	666	2144.3257	2020 - 2025	1300	4.580×10^{-22}	_	_	[113]
(210) - (010)	666	2185.2470	2060 - 2250	1639	7.630×10^{-22}	-	_	[113]
(200) - (000)	666	2201.157	2058 - 2270	1530	3.000×10^{-20}	0.0047	8–30	[139]
(021) - (000)	666	2407.9345	_	862	4.110×10^{-22}	0.002	20	[112]
(120) - (000)	666	2486.5766	_	1042	4.730×10^{-22}	0.002	20	[112]
(012) – (000)	666	2726.1066	_	-	3.360×10^{-21}	0.001	4–10	[111]
(111) - (000)	666	2785.2446	2735 - 2807	1449	3.140×10^{-20}	0.004	5–25	[139]
(210) - (000)	666	2886.1781	_	_	1.150×10^{-21}	0.001	4–10	[111]
(003) - (000)	666	3041.200	2962 - 3056	1575	1.105×10^{-19}	-	_	[139]
(102) - (000)	666	3083.7024	2900 - 3206	_	1.270×10^{-20}	0.001	8–16	[114]
(201) - (000)	666	3186.4097	2900 - 3206	-	9.340×10^{-21}	0.001	8–16	[114]
(013) – (000)	666	3697	3600 - 3900	_	6.150×10^{-21}	0.002	8–17	[116]
(112)-(000)	666	3743	3600 - 3900	_	1.380×10^{-22}	0.002	8–17	[116]

 $^{a}\, The \ code \ 666 \ stands \ for \ ^{16}O_{3}, \ 888 \ for \ ^{18}O_{3}, \ 688 \ for \ ^{16}O^{18}O^{18}O, \ etc.$

Table 7. Vibrational spectroscopic constants of the ozone molecule: zero-point frequencies ω_i , anharmonicity constants x_{ij} , and Darling–Dennison resonance constants γ_{DD} (cm⁻¹) [254].

Constant	¹⁶ O ₃	¹⁸ O ₃	¹⁶ O ¹⁸ O ¹⁶ O	¹⁸ O ¹⁶ O ¹⁸ O	¹⁶ O ¹⁶ O ¹⁸ O	¹⁸ O ¹⁸ O ¹⁶ O
$\overline{\omega_1}$	1134.90	1069.85	1105.75	1100.91	1122.35	1092.08
ω_2	716.00	674.96	707.07	682.77	699.51	691.14
ω_3	1089.20	1026.77	1052.69	1064.17	1072.30	1035.52
<i>x</i> ₁₁	-4.9	-4.4	-5.1	-4.2	-9.1	-8.6
<i>x</i> ₁₂	-9.1	-8.1	-8.1	-8.9	-9.6	-8.6
<i>x</i> ₁₃	-34.8	-30.9	-34.2	-31.5	-19.0	-20.5
<i>x</i> ₂₂	-1.0	-0.9	-1.0	-0.9	-1.0	-0.9
<i>x</i> ₂₃	-17.0	-15.1	-15.5	-16.5	-16.2	-14.9
x ₃₃	-10.6	-9.4	-9.7	-10.3	-13.0	-11.7
γ _{DD}	26.92	23.92	26.08	24.76	11.22	12.63

K_{ijk} , K_{ijkl}	¹⁶ O ₃	¹⁸ O ₃	${}^{16}\mathbf{O}^{18}\mathbf{O}^{16}\mathbf{O}$	$^{18}O^{16}O^{18}O$	${}^{16}\mathbf{O}{}^{16}\mathbf{O}{}^{18}\mathbf{O}$	18 O 18 O 16 O
<i>K</i> ₁₁₁	-49.50	-45.31	-48.86	-46.02	-61.58	-58.56
K ₁₁₂	-27.72	-25.37	-25.22	-27.78	-28.77	-25.60
K ₁₁₃	0	0	0	0	-78.26	-71.19
K ₁₂₂	-29.64	-27.13	-29.92	-26.84	-26.71	-27.24
K ₁₂₃	0	0	0	0	-11.58	-7.24
K ₁₃₃	-223.74	-204.78	-215.81	-212.70	-164.03	-165.65
K ₂₂₂	-19.06	-17.44	-17.80	-18.55	-18.85	-17.66
K ₂₂₃	0	0	0	0	9.25	8.52
K ₂₃₃	-53.59	-49.04	-45.25	-57.02	-54.37	-46.93
K ₃₃₃	0	0	0	0	57.96	51.95
K ₁₁₁₁	2.47	2.19	2.27	2.37	4.37	3.84
K ₁₁₁₂	-1.36	-1.20	-1.64	-0.88	-0.53	-1.14
K ₁₁₁₃	0	0	0	0	11.12	10.09
K ₁₁₂₂	-0.98	-0.87	-0.34	-1.42	-1.72	-1.08
K ₁₁₂₃	0	0	0	0	3.45	2.41
K ₁₁₃₃	27.81	24.71	26.27	26.20	18.14	18.24
K ₁₂₂₂	3.27	2.90	3.31	2.81	2.97	3.05
K ₁₂₂₃	0	0	0	0	-2.82	-2.82
K ₁₂₃₃	5.42	4.81	3.22	6.92	3.68	2.36
K ₁₃₃₃	0	0	0	0	-6.21	-5.64
K ₂₂₂₂	0.64	0.57	0.52	0.67	0.65	0.55
K ₂₂₂₃	0	0	0	0	-0.70	-0.65
K ₂₂₃₃	-5.56	-5.29	-5.75	-5.44	-5.17	-5.05
K ₂₃₃₃	0	0	0	0	-2.44	-1.78
K ₃₃₃₃	6.16	5.47	5.81	5.81	6.98	6.44

Table 8. Cubic (K_{ijk}) and quartic (K_{ijkl}) potential constants of the ozone molecule (cm⁻¹) [254].

Table 9. Rotational and centrifugal constants (Watson-type Hamiltonian parameters) of the lower vibrational states of ¹⁶O₃ (cm⁻¹) [106–108, 253].

Constant	(000)	(010)	(001)	(100)	(020)
Ā	3.5512082	3.604597	3.5005 530	3.5566937	3.6598873
В	0.4449752	0.4437146	0.4412960	0.4427365	0.4424384
С	0.3944787	0.3921676	0.39099828	0.3925682	0.3898023
$10^3 \Delta_K$	0.2115182	0.2325631	0.2080726	0.2174947	0.255772
$10^5 \Delta_{KJ}$	-0.1845637	-0.1789187	-0.1697694	-0.2156916	-0.1714333
$10^6 \Delta_J$	0.4539087	0.45671	0.4566971	0.4614806	0.4598267
$10^5 \delta_K$	0.322875	0.3885923	0.2960915	0.3557001	0.4588133
$10^7 \delta_J$	0.6974667	0.6921277	0.7595127	0.6587752	0.6858133
$10^{7}H_{K}$	0.3932967	0.4820867	0.3903567	0.4189690	0.5803
$10^{8}H_{KJ}$	-0.1845	-0.2100433	0.180230	-0.204093	-0.2494333
$10^{10} H_{JK}$	-0.0708333	0.0243667	0.01594	-0.31221	0.1743333
$10^{12}H_J$	0.3453333	0.2932667	0.170404	0.42363	0.1883333
$10^{8}h_{K}$	0.2149	0.317933	0.24824	0.09785	0.4353333
$10^{11}h_{KJ}$	-0.758333	-1.147667	-1.14199	-0.7998	-1.87
$10^{13}h_J$	1.7635	1.8596666	2.35510	0.91643	2.1133333
$10^{10}L_{K}$	-0.103063	-0.1348633	-0.114128	-0.121887	-0.1498
$10^{14} L_{JK}$	1.3766667	0.826666	-	-	_
$10^{12} L_{KKJ}$	0.4183333	0.5303333	0.31737	0.30859	1.1666666
$10^{15} L_{KJJ}$	_	-	-0.3251	-0.3251	_
$10^{17}L_J$	-	-	0.2994	0.2994	_
$10^{12} l_K$	1.34333	1.34333	0.2107	0.1455	1.34333
$10^{14} l_{KJ}$	3.043333	3.043333	-	-	3.043333
$10^{14} P_K$	0.2296667	0.2296667	0.333	0.333	0.2296667
$10^{15} P_{KKKJ}$	-0.174667	-0.174667	0.1895	0.1895	-0.174667

Table 9. continued

Constant	(011)	(110)	(002)	(200)	(101)
Ā	3.5523057	3.6108121	3.4488313	3.5598218	3.5019861
В	0.4398971	0.4414462	0.4374296	0.4400888	0.4385779
С	0.3885034	0.3902987	0.3878652	0.3900886	0.3882662
$10^3 \Delta_K$	0.2286541	0.2397279	0.2045468	0.2239403	0.2138455
$10^5 \Delta_{KJ}$	-0.159822	-0.207525	0.142556	-0.264145	-0.186964
$10^6 \Delta_J$	0.4598571	0.466893	0.467275	0.465791	0.460896
$10^5 \delta_K$	0.349531	0.432119	0.207537	0.350975	0.433010
$10^7 \delta_J$	0.760992	0.647274	0.788628	0.625022	0.748215
$10^{7}H_{K}$	0.46448	0.499650	0.38227	0.46775	0.408511
$10^{8}H_{KI}$	-0.187597	-0.210352	-0.147366	0.240487	-0.21730
$10^{10}H_{JK}$	-0.31110	-0.8376	_	-0.5746	-0.2205
$10^{12}H_{J}$	0.11362	0.16922	0.3215	0.3215	0.3215
$10^{8}h_{K}$	_	-0.2793	0.32689	0.14276	0.20764
$10^{11}h_{KJ}$	_	-3.301	-0.7576	-0.7576	-0.7576
$10^{13}h_J$	1.9999	0.9160	1.755	1.755	1.755
$10^{10}L_{K}$	-0.10762	-0.12635	-0.10353	-0.19126	-0.110623
$10^{14}L_{JK}$	-	-	-	_	_
$10^{12}L_{KKI}$	0.2739	0.2739	0.2739	0.2739	0.2739
$10^{15} L_{KJJ}$	-0.3251	-0.3251	-0.3251	-0.3251	-0.3251
$10^{17}L_J$	0.2994	0.2994	0.2994	0.2994	0.2994
$10^{12} l_K$	0.1812	0.1812	0.1812	0.1812	0.1812
$10^{14} l_{KJ}$	_	_	_	_	_
$10^{14} P_K$	0.333	0.333	0.333	0.333	0.333
$10^{15} P_{KKKJ}$	0.1895	0.1895	0.1895	0.1895	0.1895

Table 10. Rotational and centrifugal constants (Watson-type Hamiltonian parameters) of the (000) state for different isotopic modifications of ozone (cm^{-1}) [109, 115].

Constant	¹⁶ O ¹⁶ O ¹⁸ O	¹⁶ O ¹⁸ O ¹⁶ O	¹⁸ O ₃	¹⁸ O ¹⁶ O ¹⁸ O	¹⁸ O ¹⁸ O ¹⁶ O
A	3.4881 85078	3.29049002	3.1584962	3.4216748	3.2250621
В	0.420008328	0.4453 9923	0.3958952	0.3957901	0.4200689
С	0.37400894	0.39132966	0.3510010	0.3539743	0.3707796
$10^3 \Delta_K$	0.20388458	0.18088118	0.1668257	0.1962563	0.17383045
$10^5 \Delta_{KJ}$	-0.1902291	-0.1317952	-0.1460178	-0.194257	-0.1394931
$10^6 \Delta_J$	0.40691789	0.4478478	0.35843065	0.3637897	0.4010435
$10^5 \delta_K$	0.2920551	0.3115599	0.2536020	0.2631333	0.2815496
$10^7 \delta_J$	0.6060594	0.7290516	0.5506050	0.5252111	0.6341487
$10^{7}H_{K}$	0.3520083	0.2955062	0.277090	0.339410	0.297244
$10^{8}H_{KJ}$	-0.158923	-0.147549	-0.124992	-0.149597	-0.138661
$10^{11}H_{JK}$	-1.4066	-1.2117	-0.100537	-0.7843	-0.9306
$10^{12}H_J$	0.30051	0.43919	0.24327	0.28697	0.33583
$10^{8}h_{K}$	0.15996	0.16147	0.13530	0.15749	0.15319
$10^{13}h_J$	1.1280	1.6029	0.9627	1.1080	1.3012
$10^{11}L_{K}$	_	_	-0.6299	-0.4706	-0.73694
$10^{11}h_{KJ}$	0.2081	0.1181	_	—	—

Table 11.	Darling-Dennison resonance interaction constants for	¹⁶ O ₃	(cm^{-1})).
Tuble III	Burning Bennison resonance interaction constants for	03	(em	,

v	v′	$h_{\nu\nu'}^{DD}$	$10^3 h_{\nu\nu'}^{\prime DD}$	$10^4 h_{\nu\nu'}^{\prime\prime DD}$	$10^3 h_{\nu\nu'}^{mDD}$	Ref.
(200)	(002)	-27.0	1.146	-3.8448	_	[108]
(012)	(210)	-27.0	_	_	_	[111]
(201)	(003)	-46.8	_	_	0.9025	[114]

v	v′	$10^2 h_{\nu\nu'}^c$	$h_{\nu\nu'}^{\prime c}$	$10^6 h''_{\nu\nu'}$	$10^6 h_{\nu\nu'}^{\prime\prime\prime c}$	$10^8 h_{\nu\nu'}^{\prime\prime\prime\prime c}$	R ef.	
(001)	(100)	-0.99630187	-0.470	0.756880	-0.1058506	0.05842	[253]	
(110)	(011)	-1.009976	-0.470	0.85510	-0.106248	-0.5931	[106]	
(101)	(002)	-1.58287	0.664626	2.01482	-0.02436	-	[108]	
(101)	(200)	-1.545312	-0.66468 0.6742811	1.16703 —	-0.25132 1.03787	_	[108] [111]	
(111)	(012)	-1.679259	-0.6602737	_	-1.35213	_	[111]	
(111)	(210)	-1.528501	-0.470	-	-	_	[112]	
(021)	(120)	-1.055102	0.31	_	_	_	[116]	
(112)	(013)	-1.654548	0.31	_	_	_	[114]	
(102)	(003)	-1.233	_	-	—	_	[114]	
(201)	(102)	-0.6394						

Table 12. Coriolis resonance interaction constants for ${}^{16}O_3$ (cm⁻¹).

Table 13. Experimental absorption cross section in O₃ (in units of 10^{-19} cm² per molecule) for 9*P* lines of CO₂-laser radiation for different total pressures in the ozone-air mixture; T = 298 K [130].

Laser line	Pressure/Torr								
	75	150	270	355	475	735			
P(8)	11.2	_	_	6.50	_	5.75			
P(10)	0.50	0.76	1.24	-	1.88	2.63			
P(12)	11.6	8.05	6.26	6.01	5.30	5.06			
P(14)	2.5	3.20	3.66	4.49	4.82	5.30			
P(16)	1.20	1.69	2.25	2.81	2.95	3.59			
P(18)	2.9	3.20	3.06	2.96	2.69	2.50			
P(20)	1.04	1.47	1.83	1.94	1.89	1.77			
P(22)	0.15	0.33	0.63	0.64	0.66	0.79			
P(24)	0.20	0.22	0.24	0.25	0.26	0.29			



Figure 7. Comparison of measurements of ozone absorption coefficients for the various lines in 9.6 μ m CO₂-laser radiation made by: (1) Pattey et al. [127]; (2) Shewchun et al. [128].

the coefficients of absorption of different frequencies of CO_2 -laser radiation by ozone [93, 127–134] (Fig. 7 and Table 13), including those with smooth frequency tuning [93, 129–134]. A characteristic feature of this stage

of development of the spectroscopy of ozone (and not only ozone) was the setting up of computer databases contain-ing the parameters of the spectral lines of atmospheric gases. Such 'computer atlases' of lines considerably extend the feasibility of calculations in applied spectroscopy and also facilitate the interpretation of experiments on the absorption of radiation by gaseous media. The first database (the so-called McClatchey atlas) was set up in AFCRL (USA) in 1973 and contained, as a constituent part, the parameters of ozone lines. The contents of databases are periodically enlarged and revised. Up-to-date data on the parameters of the rotational and vibrational-rotational lines of ozone are contained in the databases space AFGL [135–137], HITRAN [119, 139], GEISA [138], etc. The number of ozone lines included in the databases is increasing steadily owing to the addition of lines with high rotational quantum numbers, weakly forbidden lines, and lines belonging to 'hot' bands. For example, in the version HITRAN 1986 [139] there are 20 969 vibrational-rotational transitions of ozone in the 10 µm region but the version HITRAN 1990 [119] contains 53 735 such lines. In 1990 Flaud et al. [140] published in book from an atlas of the spectral lines of ozone in the microwave and infrared regions $(0-3400 \text{ cm}^{-1})$ in which up-to-date results on the high-resolution spectroscopy of O₃ are arranged systematically. But, the data collected there [140] do not cover the whole infrared range. In particular, there are also ozone lines in the near-IR region ($\lambda \approx 1 \ \mu m$) but they are due to transitions from excited electronic states and they have not been studied adequately. The rotational structure of such spectra is currently being investigated actively (see, for example, Refs [141] and [142]).

The development of laser technology and sub-Doppler saturation spectroscopy methods has enabled lasers to study Stark and Zeeman effects in vibrational-rotational transitions. Such studies have been applied to ozone [143], the Zeeman effect being observed for two vibrational-rotational transitions of the (000) - (001) band with the help of a CO₂ laser. The ozone molecule is an extremely suitable subject for perfecting the laser magnetic resonance technique (as it has a small rotational magnetic moment, several good resonances with CO₂-laser frequencies, etc.).

Advances in the high-resolution IR spectroscopy of ozone enabled lasers to be used for monitoring ozone in the atmosphere as long ago as the late 1970s. In 1977 Menzies and Shumate [144] used continuous CO_2 -laser radiation with a wavelength of 9.6 μ m to make the first remote measurements of ozone concentration and in 1978 a

pulsed CO_2 laser was used for the same purpose [145]. Concurrently there was a considerable improvement in the technique of the already routine infrared and microwave measurements of the altitude distribution of ozone in the atmosphere [146–152]. Traditional measurements of ozone concentration in the IR region were increasingly carried out with the use of high-resolution spectrometers [151, 152]. Surveys of modern methods (including optical methods) for investigating atmospheric ozone have been published [153–155]. Recent studies of atmospheric ozone have led to the discovery of anomalous enrichment of the stratosphere in ${}^{16}O^{18}O$ and ${}^{16}O^{18}O^{16}$ molecules [156], an effect which is still not entirely clear. This has given a considerable stimulus to studies of the vibrational–rotational spectra of isotopic modifications of ozone.

A complex and subtle aspect in studies of the rotational structure of ozone absorption bands is the extraction of information on the collision broadening and shift of individual spectral lines. Measurements and calculations

Table 14. Collision half-widths γ of vibrational-rotational lines of ${}^{16}O_3$.

Mixture	$(\gamma \pm \Delta \gamma)/cm^{-1} atm^{-1}$	T/K	R ef.	Remarks
$\overline{O_3 - O_3}$	$0.106 - 0.126, \pm (0.002 - 0.006)$	292	[161]	7 lines in rotational spectrum, $75 - 120$ GHz, $J \leq 22$, $K_a \leq 3$
$O_3 - O_3$	$0.07 - 0.16, \pm (0.005 - 0.04)$	296	[160]	14 lines $v_1 + v_3$, 2084.1–2085.1 cm ⁻¹ , $J = 19-26$, $K_a \le 13$
$O_3 - O_3$	$0.11 - 0.12, \pm 0.01$	296	[160]	8 lines $v_1 + v_2 + v_3$, 2775.84–2776.39 cm ⁻¹ , $J = 10, K_a \leq 7$
$O_3 - O_3$	0.104 - 0.127	300	[173]	by calculation, $J \leq 34$, $K_a \leq 15$, A-type bands
$O_3 - O_3$	0.108 - 0.11	300	[173]	by calculation, $J \leq 34$, $K_a \leq 15$, B-type bands
$O_3 - O_3$	0.144	285	[157]	1 line v_1 , 1129.442 cm ⁻¹
$O_3 - O_3$	$0.0820 - 0.1164, \pm (5 - 14)\%$	296	[170]	79 lines v_2 , 47 lines v_1 , 189 lines $v_2 + v_3$, 33 lines $v_1 + v_3$, 7 lines $2v_3$, 4.8–17 µm
$O_3 - O_3$	$0.0841 - 0.125, \pm (0.002 - 0.008)$	296	[167]	15 lines v_3 , 1015.4393 – 1058.3232 cm ⁻¹ , $J \leq 27$, $K_a \leq 12$
$O_3 - O_3$	$0.0839 - 0.1143, \pm 4\%$	296	[169]	213 lines $v_1 + v_3$, 2060.3402 – 2134.2753 cm ⁻¹ , $J = 2-45$, $K_a \leq 13$
$O_3 - O_3$	$0.0972 - 0.1031, \pm 4\%$	296	[169]	16 lines $2v_1$, 2171.1712 – 2187.5270 cm ⁻¹ , $J = 18$ –39, $K_a \le 1$
$O_3 - O_3$	$0.0861 - 0.1054, \pm 4\%$	296	[169]	8 lines $2v_3$, 2066.8278 – 2122.2309 cm ⁻¹ , $J = 15-32$, $K_a \leq 9$
$O_3 - O_3$	$0.107 - 0.125, \pm (0.002 - 0.004)$	292	[163]	3 lines in rotational spectrum, $93.95 - 101.74$ GHz, $J = 2, 4, 14, K_a = 0, 2$
$O_3 - O_2$	$0.069 - 0.078, \pm (0.002 - 0.003)$	292	[163]	3 lines in rotational spectrum, $93.95 - 101.74 \text{ GHz}$, $J = 2, 4, 14, K_a = 0, 2$
$O_3 - O_2$	$0.053 - 0.058, \pm (0.002 - 0.005)$	296	[160]	9 lines $v_1 + v_3$, 2084.1–2085.1 cm ⁻¹ , $J = 21-26$, $K_a \leq 11$
$O_3 - O_2$	0.08-0.1	298	[130]	5 lines v_3 , 1043.189–1053.9192 cm ⁻¹
$O_3 - O_2$	$0.0610 - 0.0734, \pm (0.002 - 0.004)$	296	[164]	4 lines in rotational spectrum, $101.7 - 110.8$ GHz, $J \leq 29$, $K_a \leq 4$
$0_3 - 0_2$	0.0505 - 0.0568	296	[175]	by calculation, 127 lines v_3 , $J \leq 28$, $K_a \leq 11$
$0_{3} - 0_{2}$	0.0508 - 0.0556	296	[175]	by calculation, 9 lines $v_1 + v_3$, $J = 20-25$, $K_a \leq 11$
$0_{3} - 0_{2}$	0.0607 - 0.0789	296	[176]	rotational spectrum, by calculation, 6 lines, $J \leq 29$, $K_a \leq 4$
$0_{3}-0_{2}$	0.035 - 0.038	300	[173]	by calculation, $J \leq 34$, $K_a \leq 15$, A-type bands
$0_{3}-0_{2}$	0.034 - 0.038	300	[173]	by calculation, $J \leq 34$, $K_a \leq 15$, B-type bands
$O_3 - N_2$	0.058 - 0.092	293	[172]	rotational spectrum, by calculation, 18 lines, $J = 20-35$
$O_3 - N_2$	$0.067 - 0.072, \pm (0.001 - 0.003)$	296	[160]	9 lines $v_1 + v_3$, 2084, 1–2085, 1 cm ⁻¹ , $J = 21-26$, $K_a \le 11$
$O_3 - N_2$	0.061-0.07	300	[172]	by calculation, $J \leq 34$, $K_a \leq 15$, A-type bands
$O_3 - N_2$	0.058 - 0.07	300	[172]	by calculation, $J \leq 34$, $K_a \leq 15$. B-type bands
$O_3 - N_2$	0.0543 - 0.0992	292	[162]	156 lines (predominantly v_3), 987.214–1139.050 cm ⁻¹ , $J \le 52$, $K_a \le 10$
$O_3 - N_2$	0.0986-0.1166	220	[168]	33 lines v_3 , 1025.0560 – 1053.6083 cm ⁻¹ , $J = 13-20$, $K_a \le 9$
$O_3 - N_2$	$0.076 - 0.090, \pm (0.001 - 0.003)$	292	[163]	3 lines in rotational spectrum, 93.95–101.74 GHz, $J = 2, 4, 14, K_a = 0, 2$
$O_3 - N_2$	0.0741 - 0.0842	296	[164]	4 lines in rotational spectrum, $101.7-110.8 \text{ GHz}$, $J \leq 29$, $K_a \leq 4$
$O_3 - N_2$	0.0676 - 0.0793	296	[175]	by calculation, 127 lines v_3 , $J \le 28$, $K_a \le 11$
$O_3 - N_2$	0.0681 - 0.0714	296	[175]	by calculation, 9 lines $v_1 + v_3$, $J = 20-25$, $K_a \le 11$
$O_3 - N_2$	0.0726 - 0.0887	296	[176]	rotational spectrum, by calculation, 6 lines, $J \leq 29$, $K_a \leq 4$
$O_3 - N_2$	$0.0551 - 0.0907$, $\pm (2 - 6)$ %	300	[165]	60 lines v_1 , 6 lines v_2 , 1070,9898–1139.05 cm ⁻¹ , $J = 9-55$, $K_a \le 10$
$O_3 - N_2$	0.059-0.081	296	[174]	rotational spectrum, by calculation, $J \leq 35$, $K_a \leq 35$
$O_3 - air$	0.078	293	[43]	v_2 , estimated from spectrum with low resolution
O ₃ -air	$0.118, \pm 0.004$	296	[172]	2 lines in rotational spectrum, 118.3 and 110.8 GHz
$O_3 - air$	0.082	295	[128]	v_2 , 1031.4 – 1057.3 cm ⁻¹
$O_3 - air$	0.1 - 0.121	298	[130]	$5 \text{ lines } v_2$, 1043, 189 – 1053, 9192 cm ⁻¹
O_3 – air	0.07 - 0.1125 + 5%	296	[158]	11 lines v_1 998 749 – 1129 429 cm ⁻¹ $J = 9-46 K_2 \le 11$
$O_3 - air$	0.071 - 0.0961 + 5%	296	[158]	18 lines v_2 , 998,749 – 1129,429 cm ⁻¹ , $J = 9-50$, $K_a \le 14$
O_3 air	0.0610 - 0.0841	296	[159]	11 lines v_1 , 5 lines v_2 , 1069,249–1104,032 cm ⁻¹ , $J = 9$ –60, $K_2 \le 10$
$O_2 - air$	0.0637 - 0.0755	296	[175]	by calculation 127 lines v_2 , $I \le 28$, $K \le 11$
$\Omega_2 - air$	0.0644 - 0.0678	296	[175]	by calculation 9 lines $v_1 + v_2$ $I = 20-25$ $K \le 11$
O_2 air	0.063 - 0.068	296	[160]	9 lines $v_1 + v_2$ 2084 1–2085 1 cm ⁻¹ $I = 21-26$ $K \le 11$
O ₂ _air	0.003 - 0.000	300	[173]	by calculation $I \leq 34$ K ≤ 15 A-type bands
$O_2 = air$	0.067 - 0.086	300	[173]	by calculation $J \leq 34$ K ≤ 15 B-type bands
$O_2 = air$	0.0539 - 0.0929 + (2 - 6) %	300	[165]	60 lines v_1 6 lines v_2 1070 9898–1139 05 cm ⁻¹ $I = 9-55$ $K < 10$
$O_2 = air$	$0.055 - 0.0525, \pm (2 - 0).70$	296	[174]	rotational spectrum by calculation $I < 35$ K < 35
O ₂ _air	0.076-0.086 + (0.0005-0.005)	290	[163]	3 lines in rotational spectrum 93 95–101 74 GHz $I = 2.4$ 14 $K = 0.2$
03-an	$0.070 - 0.000, \pm (0.0003 - 0.003)$	292	[103]	$J = 1012, J = 2, 4, 14, K_a = 0, 2$

of the shapes, widths, and shifts of O_3 lines are of interest primarily as regards applications to atmospheric optics and also regarding the study of intermolecular interactions.

Although an estimate of the collision width of O₃ lines $(0.156 \text{ cm}^{-1} \text{ atm}^{-1} \text{ for an ozone-air mixture})$ was made as long ago as 1955 by Walshaw [43], direct measurements [73, 128, 130 - 134, 157 - 171 and calculations [171 - 177] of this quantity came much later. For a long time, pressure-induced shifts of O₃ lines were not investigated at all because of the inadequate resolving power of the spectrometers. Shifts in the O₃ lines were first detected in the rotational (millimetre) spectrum by Monnanteuil and Colmont in 1983 [161]. The first calculations of the shifts in the rotational lines of O₃ were performed by Gamache and Rothman in 1985 [174] but the first experimental results for the IR range were not published until 1988 [165] and concerned mainly the lines in the v_1 band. More recently shifts of more than 150 lines in the $v_1 + v_3$ band in the 2050-2150 cm⁻¹ range have been measured [177] and empirical formulas for calculating the shifts as a function of the rotational quantum numbers proposed. Data on the collision widths of O₃ lines are a constituent part of the above-mentioned databases containing parameters of the spectral line of atmospheric gases [119, 135-139]. There is the future prospect that the databases will also contain all the information currently available on the shifts of O₃ lines. It should be pointed out that, up to the present, theoretical calculations of the collision widths of ozone lines have been carried out within the confines of various modifications of the impact theory proposed by Anderson as far back as 1949 [178]. Up to the early 1980s mainly the Anderson-Tsao-Curnutte procedure developed in 1962 [179] was being used. The data currently available on the collision broadening of ozone lines are assembled in Table 14.

Interesting results concerning collision-induced selfbroadening of ozone lines and rotational (energy) transfer have recently been obtained by Flannery et al. [166, 167]. The first direct measurement of the rotational relaxation time of lines O_3 was made by the IR double-resonance method with time resolution [166] and it was shown that rotationally inelastic collisions make only a 60% - 70%contribution to the line broadening [167].

A few words need to be said specifically about the development of the Raman spectroscopy of ozone. The first attempt to obtain the vibrational Raman spectrum of ozone was made as long ago as 1932 by Sutherland and Gerhard [180] but owing to the extremely small Raman scattering cross section as compared to the absorption cross section of O_3 in the IR region and the inadequacy of the experimental technique it was not possible to investigate the Raman spectrum at that time. More soundly based studies were carried out much later [181 - 183]. The spectrum obtained by Selig and Claassen [181] contained bands with shifts of 1103.3 and 702.1 cm^{-1} relative to the frequency of the exciting radiation, corresponding to the v_1 and v_2 vibrations of O_3 . The Raman scattering cross section in the v_1 mode for excitation with the frequency 19430 cm⁻¹ ($\lambda = 514.5$ nm) was first measured by Fouche and Chang [182]. More accurate data on Raman scattering cross sections in ozone were obtained by Schwiesow and Abshire [183], who measured the cross sections for four excitation frequencies of an argon laser in the range 19430-20891 cm⁻¹ and analysed the polarisation of the scattered radiation (Table 15). In the frequency range investigated the relative

Table 15. Relative cross sections of spontaneous Raman scattering of visible light in ozone and degree of depolarisation of the scattered radiation [183] $[\sigma_{N_2} \approx (4.3 \pm 2) \times 10^{-31} \text{ cm}^2 \text{ sr}^{-1}$; this value corresponds to the Q-branch of the 0–1 vibrational transition of N₂ for the exciting radiation wavelength $\lambda \approx 514.5$ nm].

Laser frequency/cm ⁻¹	$\sigma_{\rm O_3}/\sigma_{\rm N_2}(\pm 12\%)$	$\delta_p(\pm 0.01)$
20891	2.3	0.05
20487	2.5	0.03
20135	2.8	0.04
19430	2.2	0.10

Raman scattering cross sections were found to be almost constant. The intensities of the Raman lines corresponding to the totally symmetric v_1 and v_2 vibrations of O₃ have also been investigated [184]. The Raman scattering cross sections for a number of gases in the atmosphere (including ozone) have been obtained [185] using excitation of the gases by radiation from a KrF laser ($\lambda = 248.5$ nm). Resonance enhancement of the scattering cross section was observed for ozone and oxygen. Resonance Raman scattering is a promising method of obtain-ing information on the highly placed levels of the O₃ molecule, owing to the large cross sections (see, for example, Refs [25, 186-188]). The resonance Raman spectrum in ozone for the supply wavelength $\lambda = 266 \,\mu\text{m}$, corresponding to the Hartley band, was obtained experimentally by Imre et al. [25]. It contains vibrational bands in the $2.7-3.35 \ \mu m$ range, enabling the positions of many highly placed levels of O₃ to be determined. However, as studies of the resonance Raman scattering of ozone are a topic belonging to ultraviolet, rather than infrared, spectroscopy they deserve only a brief mention here.

3.2 Nonlinear spectroscopy

The appearance of high-power CO₂ lasers stimulated the creation of a new branch of ozone spectroscopy: nonlinear laser IR spectroscopy. The numerous effects accompanying the action of intense laser radiation on ozone, viz. absorption saturation, cascade and many-photon excitation, stimulation of dissociation and chemical reactions, generation of harmonics, etc., became the subject of detailed studies. The development of the nonlinear spectroscopy of ozone was to a considerable extent due to the keen interest in the early 1970s in the control of chemical reactions with the help of laser radiation, bondselective photochemistry, and the collisionless dissociation of molecules. However this was not the only reason for the interest in the nonlinear IR spectroscopy of ozone. The O₃ molecule is a suitable subject for the study of processes taking place in triatomic molecules under the influence of strong laser fields; these processes possess a whole series of distinctive features compared with similar processes in diatomic and large polyatomic molecules. Ozone differs from other triatomic molecules in having the following important properties: (1) a low dissociation energy, (2) a high density of vibrational-rotational levels, and (3) strong resonance absorption of 9.6 µm CO₂ laser radiation. It is these properties taken together that make ozone, in spite of its chemical instability, a suitable subject for studying the behaviour of triatomic molecules in strong laser IR fields.

Radiation from high-power pulsed CO_2 lasers was used as long ago as the early 1970s for the selective excitation of the (001) state of ozone with the aim of studying temperature dynamics during the subsequent relaxation of the vibrational energy. This method was used to measure the rates of intramode, intermode, and vibrational-translational relaxation in ozone [189–191]. Later on the IR doubleresonance method came into use for the study of relaxation processes in ozone [192–194]. In experiments with pure ozone [192] it was found that the intermode exchange v_1 , $v_3 - v_2$ proceeds almost twice as fast as had previously been judged from the results of Rosen et al. [189–191]. Similar measurements of relaxation rates were made in the presence of the buffer gases O_2 , N_2 , and Ar [193, 194].

With the development of laser technology attempts were made to obtain laser generation in various gases including ozone. Laser generation in ozone (in an $O_3 - N_2$ mixture) was achieved for the wavelengths 6.60, 8.49, 9.01, and 9.06 µm in 1968 [195].

An attempt to detect the first nonlinear-optical effect in ozone (dissociation under the action of a high-power pulse form a CO₂ laser) was made in 1979 by Proch and Schroder [196] but a proper interpretation of this experiment was not obtained. The effect of vibrational excitation of O₃ by CO₂ laser radiation on the UV absorption spectrum of ozone has been studied [197-200]. It was shown that IR excitation leads to a considerable change in the UV absorption cross sections in O₃. On the basis of this a method was proposed for determining the degree of excitation and the rate of relaxation of vibrational energy in O3 using UV radiation. Subsequently the CARS-spectroscopy method came into use as a diagnostic of the populations of the ozone vibrational levels [201]. Adler-Golden et al. [200] also investigated for the first time the spectral and energy dependences of the mean number of quanta of CO₂-laser radiation absorbed by ozone and they found an absorption saturation effect at certain laser frequencies. Investigation of the saturation effect can give valuable information on the constants of the relaxation

processes and the distribution of populations among the levels. An absorption saturation effect in the v_3 mode of O_3 was observed in a low-temperature condensed phase as long ago as 1979 [202]. Relaxation times were also determined in the same work. Recently the saturation effect has also been used to measure vibrational temperatures of ozone (in an O₃-Ar mixture) [203]. Extensive theoretical and experimental studies of the excitation and dissociation of ozone by the action of a CO₂-laser pulse under collision conditions of radiation absorption have been reported [204-222]. Appreciably wider ranges of radiation frequency and power were used compared with the work of Adler-Golden et al. [200]. In particular, the maximum intensity of the CO₂-laser radiation pulses in these experiments was several $GW \text{ cm}^{-2}$. Interesting effects reported in these papers include the effect of overcoming rotational saturation ('bottleneck') in a strong laser field [208, 209, 212-214], laser-induced nonthermal explosive decomposition of ozone [213], and also the possible effective generation of the third harmonic and of the sum frequency in O_3 molecules [211, 217]. In the case of laser-induced excitation of O₃ under conditions where vibrational energy exchange is developed in an $O_3 - O_2$ mixture investigations of the energy absorbed have been made by Raffel and Wolfrum [223]. They also studied the explosive decomposition of ozone by the action of a laser pulse but in contrast to the results of Ivanov et al. [213] the explosion was thermal in character [224]. The laserinitiated thermal explosive decomposition of ozone was also studied by Mordkovich et al. [225]. Much consideration has been given to the thermal decomposition of ozone under the influence of laser IR radiation (see, for example, Refs [226-229]). Another interesting effect, which makes it possible to control chemical reactions with the aid of IR radiation, is the marked increase in the rates of bimolecular reactions of ozone when the reagents are vibrationally excited [230-234]. The collisionless many- photon excitation and dissociation of O₃ in the field of high-power IR radiation has been simulated within the framework of Hansel's classical description [235]. A more correct quantum treatment of



Figure 8. Spectrum of collisionless two-photon excitation of ozone molecules [238]. The quantity plotted on the ordinate axis is the time-averaged total population of the (002), (200), and (101) vibrational levels. The calculation was made for an irradiation intensity I = 40 GW cm⁻² and the initial temperature T = 0 K.

these phenomena taking into account the actual rotational structure of the spectrum of the vibrational levels is given in the theoretical work of Quack and Sutcliffe [236–239]. In particular they demonstrated the possible optical excitation of O_3 in a deformation (bending) mode right up to the dissociation limit [237] and the possible inversion of the vibrational-rotational populations of O_3 on multiphoton excitation [238]. As an example, the calculated spectrum of collisionless two- photon excitation of O_3 molecules is shown in Fig. 8. However, the quantitative results in these papers [236–239] should be treated with some caution because they were obtained with out-of-date spectroscopic constants.

4. The current position and prospects for development

As is clear from the above there has been undoubted progress in modern infrared and microwave spectroscopy applied to ozone. However, in comparison with other simple triatomic molecules, as for example CO₂, H₂O, and N_2O , the available information is nevertheless inadequate. For example, the rotational structure of vibrational states of ozone with the sum of the vibrational quantum numbers $v_1 + v_2 + v_3 > 4$ has hardly been studied. Data on the majority of the high vibrational levels are fragmentary, making it difficult to obtain reliable spectroscopic constants from them. Obtaining information on the highly placed states of ozone is complicated for the following reasons. It is difficult to record most of the lines in 'hot' bands because of their low intensity and making measurements at high temperatures (which is the normal procedure in such cases for stable gases) is not suitable for ozone because it decomposes rapidly under these conditions. For the same reason very little is known about the temperature dependence of collision widths and shifts of O₃ lines. In addition, in the theoretical treatment of the spectra of highly placed states allowance must be made for the resonance interaction of many states the parameters of which are not always known. In many instances such an undertaking is simply not proper.

Apart form this there is another difficulty of a fundamental character which considerably inhibits further progress in the spectroscopy of highly placed states of all molecules. This arises from the fact that the theoretical methods currently used in practice for the analysis of vibrational and vibrational-rotational spectra are based on perturbation theory. For this the potential function of a molecule is put in the form of a Taylor series expansion. This approximation works fairly well for low values of the vibrational quantum numbers v_i but as v_i increases such a model becomes less efficient, requiring higher-order terms in the expansion to be taken into account. A similar problem is encountered in using Watson's effective rotational Hamiltonians for large values of J, it again being necessary to take into consideration a considerable number of terms in the expansion. Furthermore, starting from a certain value of Jdepending on the degree of vibrational excitation, the series of the Watson Hamiltonian ceases to be convergent [240]. One of the possible ways out of this situation is to represent the Hamiltonian as an asymptotic series but such an approach has not yet been developed sufficiently. Theories employing the intramolecular potential in a closed form, i.e. without expansion in a series, are promising for the analysis of vibrational spectra.

Development of the above-mentioned new theoretical approaches is still in the initial stage. This is partly due to the paucity of data on the spectra of states close to the dissociation limit. This applies especially to the spectra of the isotopic modifications of ozone. The immediate task is therefore to accumulate experimental data which will stimulate the development of new theoretical approaches. Various methods of laser spectroscopy and nonlinear optics, which enable vibrational and vibrational-rotational states to be excited selectively, may prove to be very promising in this respect. Some of these (CARS-diagnostic, generation of the third harmonic and the sum frequency) have already been applied successfully to O_3 . Others (e.g. IR excitation of molecules by ultrashort pulses with smooth frequency change [241]) have yet to be applied to ozone. A large amount of valuable information regarding states close to the dissociation limit of O₃ may be obtained from spectroscopic diagnostics of the products of chemical reactions of ozone including photodissociation [242, 243] and recombination [27-30] reactions. A factor currently restricting the use of lasers for selective excitation of individual vibrationalrotational states is the lack of high-power, accessible generators of monochromatic radiation in the IR range with smooth frequency change.

Studies of spectroscopic manifestations of intermolecular reactions of ozone, as compared with other molecules, are also in the initial stage of development: there are as yet insufficient experimental data, few studies of the temperature dependence of line broadening and shifts, etc. The only data available for ozone are for long-range multipole interactions with certain simple molecules [172, 173] and spherically symmetric Lennard-Jones potentials for O₃-O₃ [244], $O_3 - N_2$ and $O_3 - O_2$ [176]. Nothing is known about the anisotropy of intermolecular interactions and there are no ab initio calculations. There are thus openings in a broad field of research. The need to revise traditional theories of spectral line broadening and shift (Anderson-Tsao-Curnutte and other modifications of the impact approximation) can no longer be put off. This need stems primarily from the requirement to take account of collisions of all types (elastic, inelastic, and collision complexes) and also vibrationalrotational interactions (including resonance interactions) and the details of trajectory dynamics. Some of these problems have already been actively worked out in applications to molecules, e.g. H₂O [240] and HCl [245], that have been studied to a greater extent. In this respect direct computer simulation of collisional vibrational-rotational exchange processes using the classical trajectories method [246] is also promising for ozone.

5. Conclusions

To sum up, four stages in the development of the vibrational-rotational spectroscopy of ozone can be distinguished. The first stage (from the second half of the 19th century to the end of the 1920s) is characterised by the slow accumulation of purely descriptive information on the absorption bands of ozone in the IR region and attempts to isolate the spectrum of ozone from the spectra of attendant gases which were inevitably present in the mixture as it was impossible to obtain pure ozone. No attempts were made to analyse the available spectra

because at that time only the first steps had been taken to develop the quantum mechanics of molecules. It was only at the end of this period that the world scientific community realised that the problem of atmospheric ozone should be singled out as especially important: it was not until 1929 that the first congress on atmospheric ozone was held in Paris and the International Ozone Commission set up.

The second stage in the development of the vibrationalrotational spectroscopy of ozone (beginning of the 1930s to the end of the 1940s) is associated with rapid advances in the quantum mechanics of molecules. It was characterised by numerous attempts to interpret the IR spectrum of ozone. The failure of these attempts was due primarily to over estimation of the quality of the experimental data available at that time, in spite of successes in obtaining almost pure ozone. The level of development of spectroscopic experimental technique did not match the significantly improved level of development of theory. This second period also saw the first measurements of the dipole moment of the O₃ molecule and direct measurements of its geometrical parameters, as well as the first use of the IR region for optical monitoring of atmospheric ozone. Although there was considerably greater activity in research on ozone than in the first stage, the second stage did not give reliable results, but is conventionally regarded as preparatory.

The third stage (end of the 1940s to the beginning of the 1970s) is marked by significant advances in the study of ozone because of the development both of spectroscopic technique and of theoretical and calculating methods. There was a rapid development in microwave spectroscopy, enabling much valuable information to be obtained. It was only at this stage that serious investigations of the rotational structure of ozone bands, including the collision broadening of individual lines, became possible. The first remote measurements of the ozone content of the atmosphere were made by using microwave measurements and substantially improving the techniques of IR measurements.

The fourth stage started approximately in the mid-1970s and continues to the present day. By this time the ozone problem has to a significant extent moved from the sphere of science to that of economics and politics [247] and this has given a considerable stimulus to the creation of largescale research programmes [248-251]. Unprecedented interest in the O₃ molecule was generated by the discovery of ozone 'holes' in the atmosphere [252]. This fourth stage is characterised by an extreme abundance of informa- tion resulting from a new level of experimental technique (Fourier analysers, smoothly tunable laser spectrometers, wide use of computers in experiments, etc.) and the creation of computer-based spectroscopic databases. The nonlinear laser spectroscopy of ozone made its appearance and was successfully developed. Lasers have come into wide use for monitoring ozone concentrations. However the development of the theoretical ideas which had ben formed mainly in the third stage lagged behind and these ideas proved to be incapable of explaining all the various available experimental data. The current situation somewhat resembles that at the second stage but in reverse. Further advances in infrared microwave spectroscopy of ozone will evidently entail improvements in current theoretical ideas on molecular spectroscopy and the development of fundamentally new ideas, along with a wide application of experimental nonlinear optical methods (CARS-spectroscopy, generation of harmonics and composite frequencies, use of ultrashort pulses for excitation of molecules). In our opinion the development of combined experimental methods, such as double IR-UV and IR-MW resonances, is also promising. New fundamental information about ozone will also be obtained from a thorough study of the vibrationalrotational spectra of its isotopic modifications.

References

- 1. Tyndall J Contribution to Physics in the Domain of Radiant Heat (London, 1872)
- 2. Angström K Ark. Mat. Astron. Fys. 1 347 (1904)
- 3. Angström K Ark. Mat. Astron. Fys. 1 395 (1904)
- 4. Ladenburg E, Lehmann E Ann. Phys. (Leipzig) 21 305 (1906)
- 5. Gerhard S L Phys. Rev. 42 622 (1932)
- 6. Warburg E, Leithäuser G Ann. Phys. (Leipzig) 23 209 (1907)
- 7. Warburg E, Leithäuser G Ann. Phys. (Leipzig) 28 313 (1909)
- 8. Hettner G, Pohlman R, Schumacher H J Z. Phys. 91 372 (1934)
- 9. Brewer A K, Westhaver J W J. Phys. Chem. 34 1280 (1930)
- 10. Badger R M, Bonner L G Phys. Rev. 43 305 (1933)
- 11. Benedict W S Phys. Rev. 43 580 (1933)
- 12. Sutherland G B B M, Penny W G Proc. R. Soc. London Ser. A 156 678 (1936)
- 13. Adel A, Slipher V M, Fouts O Phys. Rev. 49 288 (1936)
- 14. Shand W, Spurr R A J. Am. Chem. Soc. 65 179 (1943)
- 15. Simpson D M Trans. Faraday Soc. 41 209 (1945)
- 16. Adel A, Dennison D M J. Chem. Phys. 14 379 (1946)
- 17. Simpson D M J. Chem. Phys. 15 846 (1947)
- Herzberg G Molecular Spectra and Molecular Structure Vol. 2 Infrared and Raman Spectra of Polyatomic Molecules (New York: Van Nostrand Reinhold, 1945)]
- 19. Wilson M K, Badger R M J. Chem. Phys. 16 741 (1948)
- 20. Klein M J, Cleveland F F, Meister A G J. Chem. Phys. 19 1068 (1951)
- 21. Cleveland F F, Klein M J J. Chem. Phys. 20 337 (1952)
- 22. Badger R M, Wilson M K J. Chem. Phys. 18 998 (1950)
- 23. McCaa D J, Shaw J H J. Mol. Spectrosc. 25 374 (1968)
- 24. Barbe A, Secroun C, Jouve P J. Mol. Spectrosc. 49 171 (1974)
- 25. Imre D G, Kinsey J L, Field R W, Katayama D H J. Phys. Chem. 86 2564 (1982)
- 26. Rawlins W T, Armstrong R A J. Chem. Phys. 87 5202 (1987)
- 27. Rawlins W T, Caledonia G E, Armstrong R A J. Chem. Phys.
- 87 5209 (1987)
 28. Adler-Golden S M, Smith D R Planet. Space Sci. 38 1121
- (1990)
- Adler-Golden S M, Matthew M W, Smith D R, Ratkowski A J J. Geophys. Res. A 95 15243 (1990)
- 30. Stair A T Jr, Sharma R D, Nadile R M, et al. J. Geophys. Res. A 90 9763 (1985)
- 31. Fowle F E Smithsonian Misc. Coll. 68 (8) 41 (1917)
- 32. Devaux J C. R. Acad. Sci. 193 1207 (1931)
- 33. Devaux J C. R. Acad. Sci. 198 1595 (1934)
- 34. Devaux J C. R. Acad. Sci. 201 1500 (1935)
- 35. Adel A, Slipher V M, Barker E F Phys. Rev. 47 580 (1935)
- 36. Adel A, Lampland C O Astrophys. J. 91 481 (1940)
- 37. Strong J Phys. Rev. 55 1114 (1939)
- 38. Strong J, Watanabe K Phys. Rev. 57 1049 (1940)
- 39. Strong J J. Franklin Inst. 231 121 (1941)
- 40. Vigroux E Ann. Phys. Paris 8 709 (1953)
- 41. Paetzold H K Z. Naturforsch. Teil A 11a 128 (1956)
- 42. Raschke E Beitr. Phys. Atmos. 38 (2) 97 (1965)
- 43. Walshaw C D Proc. Phys. Soc. London Sect. A 68 530 (1955)
- 44. Walshaw C D, Goody R M *Q.J.R.*. *Meteorol. Soc.* **82** 177 (1956)
- 45. Walshaw C D Q.J.R.. Meteorol. Soc. 83 315 (1957)
 46. Gal'tsev A P, in Problemy Fiziki Atmosfery (Problems of Atmospheric Physics, Ed. K Ya Kondrat'ev) (Leningrad: Leningrad State University, 1967) No. 5, pp 111-128

- 47. Strong J Phys. Rev. 54 242 (1938)
- 48. Benesch W M Phys. Rev. 76 863 (1949)
- 49. Adel A Bull. Am. Meteorol. Soc. 35 250 (1954)
- Goody R M, Walshaw C D, in *Proceedings of Toronto* Meteorological Conference, 1943 (London: Royal Meteorological Society, 1954) p. 49
- Rice M L, Thuronyi G Meteorol. Abstr. 10 759 (1959)
 Khrgian A Kh Fizika Atmosfernogo Ozona (Physics of the
- Atmospheric Ozone) (Leningrad: Gidrometeoizdat, 1973) 53. Migeotte M, Neven L, Vigroux E *Physica* (*Utrecht*) **18** 982
- (1952) 54. Kaplan L D, Migeotte M V, Neven L J. Chem. Phys. 24 1183
- (1956)
- 55. Clough S A, Kneizys F X J. Chem. Phys. 44 1855 (1966)
- 56. Barbe A, Secroun C, Jouve P, et al. J. Mol. Spectrosc. 64 (3) 343 (1977)
- 57. Vigroux E, Migeotte M, Neven L Physica (Utrecht) **19** 140, 143 (1953)
- Nexsen W E, Jr Scientific Report 1. AFCRL-TN-56-265 (Air Force Cambridge Research Center, 1956)
- 59. McCaa D J, Shaw J H Appl. Opt. 2 581 (1963)
- 60. Trajmar S, McCaa D J J. Mol. Spectrosc. 14 244 (1964)
- 61. Snider D E, Shaw J H J. Mol. Spectrosc. 44 400 (1972)
- 62. Townes C H, Schawlow A L *Microwave Spectroscopy* (New York: McGraw-Hill, 1955)
- 63. Trambarulo R, Ghosh S N, Burrus C A Jr, Gordy W J. Chem. Phys. 21 851 (1953)
- 64. Hughes R H J. Chem. Phys. 21 959 (1953)
- 65. Lewis G L, Smyth C P J. Am. Chem. Soc. 61 3063 (1939)
- 66. Epprecht G W Z. Angew. Math. Phys. 1 138 (1950)
- 67. Hughes R H J. Chem. Phys. 24 131 (1956)
- 68. Pierce L J. Chem. Phys. 24 (1) 139 (1956)
- 69. Burrus C A J. Chem. Phys. 30 976 (1959)
- 70. Gora E K J. Mol. Spectrosc. 3 78 (1959)
- 71. Gora E K Mem. Soc. R. Sci. Liege 9 73 (1964)
- 72. Tanaka T, Morino Y *J. Mol. Spectrosc.* **33** 538 (1970)
- T3. Lichtenstein M, Gallagher J J, Clough S A J. Mol. Spectrosc.
 40 10 (1971)
- Depannemaecker J C, Duterage B, Bellet J C. R. Acad. Sci. Ser. B 279 287 (1974)
 Depannemaecker J C, Duterage B, Bellet J J. Quant. Spectrosc. Radiat. Transfer 17 519 (1977)
- 75. Pochan J M, Stone R G, Flygare W H J. Chem. Phys. 51 (10) 4278 (1969)
- 76. Mack K M, Muenter J S J. Chem. Phys. 66 5278 (1977)
- 77. Meerts W L, Stolte S, Dymanus A Chem. Phys. 19 467 (1977)
- 78. Monnanteuil N, Depannemaecker J C, Bellet J, et al. J. Mol. Spectrosc. **71** 399 (1978)
- 79. Lovas F J J. Phys. Chem. Ref. Data 7 1445 (1978)
- 80. King C W, Hainer R M, Cross C P J. Chem. Phys. 11 27 (1943)
- 81. Cross C P, Hainer R M, King C W J. Chem. Phys. 12 210 (1944)
- 82. Kivelson D, Wilson E B J. Chem. Phys. 20 1575 (1952)
- 83. Watson J K G J. Chem. Phys. 45 1360 (1966)
- 84. Watson J K G J. Chem. Phys. 46 1935 (1967)
- 85. Watson J K G J. Chem. Phys. 48 181 (1968)
- 86. Watson J K G J. Chem. Phys. 48 4517 (1968)
- Caton W M, Welch W J, Silver S J. Geophys. Res. 72 6137 (1967)
- Moody H J "Millimeter wave radiometry", in Aerospace Electronics Symposium (Abstracts), Toronto, 1971 (Ottawa: Canadian Aeronautics and Space Institute, 1971) p. 1
- Harries J E, Burroughs W J Q. J. R. Meteorol. Soc. 97 519 (1971)
- 90. Naumov A P Izv. Vyssh. Ucheb. Zaved. Radiofiz. 15 682 (1972)
- 91. Kolbe W F, Buscher H, Leskovar B J. Quant. Spectrosc. Radiat. Transfer 18 47 (1977)
- 92. El-Sherbiny M, Ballik E A, Shewchun J, et al. *Appl. Opt.* **18** 1198 (1979)
- Courtois D, Thiebeaux C, Delahaigue A Int. J. Infrared Millimeter Waves 8 103 (1987)

- 94. Bellini M, De Natale P, Di Lonardo G, et al. J. Mol. Spectrosc. 152 256 (1992)
- 95. Barbe A, Secroun C, Jouve P, et al. J. Mol. Spectrosc. 75 103 (1979)
- Flaud J-M, Camy-Peyret C, Barbe A, et al. J. Mol. Spectrosc. 80 185 (1980)
- 97. Flaud J-M, Camy-Peyret C, Rothman L S Appl. Opt. 19 655 (1980)
- 98. Secroun C, Barbe A, Jouve P, et al. J. Mol. Spectrosc. **85** 8 (1981)
- 99. Barbe A, Secroun C, Jouve P, et al. J. Mol. Spectrosc. 86 286 (1981)
- 100. Goldman A, Gillis J R, Murcray D G, et al. J. Mol. Spectrosc. 96 279 (1982)
- Barbe A, Secroun C, Goldman A, Gillis J R J. Mol. Spectrosc. 100 377 (1983)
- 102. Pickett H M, Cohen E A, Margolis J S J. Mol. Spectrosc. 110 186 (1985)
- Flaud J-M, Camy-Peyret C, Malathy Devi V, et al. J. Mol. Spectrosc. 118 334 (1986)
- 104. Camy-Peyret C, Flaud J-M, Perrin A, et al. J. Mol. Spectrosc. 118 345 (1986)
- 105. Flaud J-M, Camy-Peyret C, Malathy Devi V, et al. J. Mol. Spectrosc. 122 221 (1987)
- 106. Malathy Devi V, Flaud J-M, Camy-Peyret C et al. J. Mol. Spectrosc. 125 174 (1987)
- 107. Pickett H M, Cohen E A, Brown L R, et al. J. Mol. Spectrosc. 128 151 (1988)
- 108. Rinsland C P, Smith M A H, Flaud J-M, et al. J. Mol. Spectrosc. 130 204 (1988)
- Flaud J-M, Camy-Peyret C, N'Gom A, et al. J. Mol. Spectrosc. 133 217 (1989)
- Flaud J-M, Camy-Peyret C, Rinsland C P, et al. J. Mol. Spectrosc. 134 106 (1989)
- 111. Smith M A H, Rinsland C P, Malathy Devi V, et al. J. Mol. Spectrosc. 139 171 (1990)
- Rinsland C P, Smith M A H, Malathy Devi V, et al. J. Mol. Spectrosc. 139 343 (1990)
- 113. Camy-Peyret C, Flaud J-M, Rinsland C P, et al. J. Mol. Spectrosc. 139 353 (1990)
- 114. Camy-Peyret C, Flaud J-M, Smith M A H, et al. J. Mol. Spectrosc. **141** 134 (1990)
- Perrin A, Vasserot A-M, Flaud J-M, et al. J. Mol. Spectrosc. 143 311 (1990)
- Malathy Devi V, Perrin A, Flaud J-M, et al. J. Mol. Spectrosc. 143 381 (1990)
- 117. Rinsland C P, Smith M A H, Malathy Devi V J. Mol. Spectrosc. 149 474 (1991)
- 118. Perrin A, Vasserot A-M, Flaud J-M J. Mol. Spectrosc. 149 519 (1991)
- 119. Flaud J-M, Camy-Peyret C, Malathy Devi V, et al. Appl. Opt. 29 3667 (1990)
- 120. Heyart M, Perrin A, Flaud J-M, Camy-Peyret C, et al. J. Mol. Spectrosc. 156 210 (1992)
- 121. Heyart M, Perrin A, Flaud J-M, Camy-Peyret C J. Mol. Spectrosc. 157 524 (1993)
- Carney G D, Giorgianni S, Rao K N J. Molec. Spectrosc. 80 158 (1980)
- Voitsekhovskaya O K, Makushkin Yu S, Sulakshina O N Izv. Vyssh. Uchebn. Zaved. Fiz. (9) 103 (1983) [Sov. Phys. J. 26 866 (1983)]
- 124. Adler-Golden S M, Langhoff S R, Bauschlicher C W Jr, Carney G D J. Chem. Phys. 83 255 (1985)
- 125. Carter S, Mills I M, Murrel J N, Varandas A J C Mol. Phys. 45 1053 (1982)
- 126. Steinfeld J I, Adler-Golden S M, Gallagher J W J. Phys. Chem. Ref. Data 16 911 (1987)
- 127. Patty R R., Russwurm G M, McClenny W A, Morgan D R Appl. Opt. 13 2850 (1974)
- 128. Shewchun J, Garside B K, Ballik E A, et al. Appl. Opt. 15 340 (1976)
- 129. Young C, Bunner R H L Appl. Opt. 13 1438 (1974)
- 130. Menzies R T Appl. Opt. 15 2597 (1976)

- 131. Megie G, Menzies R T Appl. Phys. Lett. 35 835 (1979)
- Lyszyk M, Depannemaecker J C, Bantegnie J G, et al. Opt. Commun. 37 53 (1981)
- 133. Kostiuk T, Hillman J J, Faris J L J. Mol. Spectrosc. **89** 397 (1981)
- 134. Sokabe N, Hammerich M, Pedersen T, et al. J. Mol. Spectrosc.
 152 420 (1992)
- 135. Rothman L S Appl. Opt. 20 791 (1981)
- 136. Rothman L S, Goldman A, Gillis J R, et al. Appl. Opt. 22 1616 (1983)
- 137. Rothman L S, Gamache R R, Barbe A, et al. Appl. Opt. 22 2247 (1983)
- Husson N, Chedin A, Scott N A, et al. Ann. Geophys. Ser. A 4 185 (1986)
- Rothman L S, Gamache R R, Goldman A, et al. Appl. Opt. 26 4058 (1987)
- 140. Flaud J -M, Camy-Peyret C, Rinsland C P, Smith M A H, Malathy Devi V Atlas of Ozone Spectral Parameters from Microwave to Medium Infrared (New York: Academic Press, 1990)
- 141. Shi J, Barker J R J. Phys. Chem. 94 8390 (1990)
- 142. Anderson S M, Hupalo P, Mauersberger K J. Chem. Phys. **99** 737 (1993)
- Schieder R, Winnewisser G Z. Naturforsch. Teil A 38 154 (1983)
- 144. Menzies R T, Shumate M S Appl. Opt. 15 2080 (1976)
- 145. Asai K, Itabe T, Igarashi T Appl. Phys. Lett. 35 60 (1979)
 146. Waters J M, Hardy J O, Jarnot R F, et al. J. Quant. Spectrosc. Radiat. Transfer 32 407 (1984); Hartmann G K, Künzi K F, Schwartz P R Mikrowellen Mag.
- 11 254 (1985)
 147. Lobsiger E, Kunzi K F, Dutsch H U J. Atmos. Terr. Phys. 46 779 (1984)
- 148. Lobsiger E J. Atmos. Terr. Phys. 49 493 (1987)
- 149. de La Noe J, Brillet J, Turati C, et al. *Planet. Space Sci.* 35 547 (1987)
- 150. Gibbins C J, Dawkins A W J, Maddison B M *Planet. Space Sci.* **36** (6) 607 (1988)
- 151. Abbas M M, Glenn M J, Kunde V G, et al. J. Geophys. Res. D: Atm os. 92 8343 (1987)
- 152. Abbas M M, Guo J, Carli B, et al. J. Geophys. Res. D: Atmos.
 92 8354 (1987)
- 153. Khrgian A Kh Meteorol. Gidrol. (5) 114 (1986)
- 154. Miller A J Planet. Space Sci. 37 1539 (1989)
- 155. McCormic M C, Zawodny J M, Veiga R E, et al. Planet. Space Sci. 37 1567 (1989)
- 156. Goldman A, Murcray F J, Murcray D J, et al. J. Geophys. Res. D: Atm os. 94 8467 (1989)
- 157. Majorana L N *Technical Report No. PTR-81-6* (Norfolk, VA: Old Dominion University, 1981)
- 158. Hoell J M Jr, Harward C N, Bair C H, Williams B S Opt. Eng. (New York) 21 548 (1982)
- 159. Lundqvist S, Margolis J, Reid J Appl. Opt. 21 3109 (1982)
- 160. Meunier C, Marche P, Barbe A J. Mol. Spectrosc. 95 271 (1982)
- Monnanteuil N, Colmont J M J. Quant. Spectrosc. Radiat. Transfer 29 131 (1983)
- Margolis J S J. Quant. Spectrosc. Radiat. Transfer 29 539 (1983)
- 163. Colmont J M, Monnanteuil N J. Mol. Spectrosc. 104 122 (1984)
- 164. Connor B J, Radford H E J. Mol. Spectrosc. 117 15 (1986)
- 165. Smith M A H, Rinsland C P, Malathy Devi V, et al. J. Opt. Soc. Am. B 5 585 (1988)
- 166. Flannery C, Mizugai Y, Steinfeld J I, Spencer M N J. Chem. Phys. 92 5164 (1990)
- 167. Flannery C, Klaassen J J, Gojer M, et al. J. Quant. Spectrosc. Radiat. Transfer 46 73 (1991)
- 168. Spencer M N, Chackerian C Jr J. Mol. Spectrosc. 146 135 (1991)
- 169. Plateaux J-J, Bouazza S, Barbe A J. Mol. Spectrosc. 146 314 (1991)

- 170. Smith M A H, Rinsland C P, Malathy Devi V, J. Mol. Spectrosc. 147 142 (1991)
 171. Bouazza A, Barbe A, Plateaux LL et al. I. Mol. Spectroscience of the state of the spectra spe
- 171. Bouazza A, Barbe A, Plateaux J-J, et al. J. Mol. Spectrosc.
 157 271 (1993)
- 172. Yamamoto G., Aoki T J. Quant. Spectrosc. Radiat. Transfer 12 227 (1972)
- 173. Tejwani G D T, Yeung E S J. Chem. Phys. 63 1513 (1975)
- 174. Gamache R R, Rothman L S Appl. Opt. 24 1651 (1985)
- 175. Gamache R R, Davies R W J. Mol. Spectrosc. 109 283 (1985)
 176. Hartmann J M, Camy-Peyret C, Flaud J-M, et al. J. Quant. Spectrosc. Radiat. Transfer 40 489 (1988)
- 177. Barbe A, Bouazza S, Plateaux J-J Appl. Opt. 30 2431 (1991)
- 178. Anderson P W Phys. Rev. 76 647 (1949)
- 179. Tsao C J, Curnutte B J. Quant. Spectrosc. Radiat. Transfer 2 41 (1962)
- 180. Sutherland G B B M, Gerhard S L Nature (London) 130 (3276) 241 (1932)
- 181. Selig H, Claassen H H Isr. J. Chem. 6 499 (1968)
- 182. Fouche D G, Chang R K Appl. Phys. Lett. 20 256 (1972)
- 183. Schwiesow R L, Abshire N L J. Appl. Phys. 44 3708 (1973)
- 184. Slepukhin A Yu, Kostyuchenko L S Opt. Spektrosk. 59 441 (1985) [Opt. Spectrosc. (USS R) 59 263 (1985)]
- 185. Buldakov M A, Ippolitov I I, Klimkin V M, et al. Opt. Spektrosk. 66 1043 (1989) [Opt. Spectrosc. (USS R) 66 609 (1989)]
- 186. Atabek O, Bourgeois M T, Jacon M J. Chem. Phys. 84 6699 (1986)
- 187. Johnson B R, Kinsey J L J. Chem. Phys. 87 1525 (1987)
- 188. Chasman D, Tannor D J, Imre D G J. Chem. Phys. 89 6667 (1988)
- 189. Rosen D I, Cool T A J. Chem. Phys. 59 6097 (1973)
- 190. Rosen D I, Cool T A J. Chem. Phys. 62 466 (1975)
- 191. Hui K-K, Rosen D I, Cool T A Chem. Phys. Lett. 32 141 (1975)
- Menard-Bourcin F, Doyennette L, Menard J J. Chem. Phys. 92 4212 (1990)
- 193. Doyennette L, Menard J, Menard-Bourcin F Chem. Phys. Lett. 170 197 (1990)
- Menard-Bourcin F, Menard J, Doyennette L J. Chem. Phys. 94 1875 (1991)
- 195. Bronfin B R, Seery D J "Nitrogen-ozone laser" USA Patent No. 3566305, filed 23 December 1968; published 23 February 1971
- 196. Proch D, Schröder H Chem. Phys. Lett. 61 426 (1979)
- 197. Adler-Golden S M, Steinfeld J I Chem. Phys. Lett. **76** 479 (1980)
- 198. McDade I C, McGrath W D Chem. Phys. Lett. 72 432 (1980)
- 199. McDade I C, McGrath W D Chem. Phys. Lett. 73 413 (1980)
- 200. Adler-Golden S M, Schweitzer E L, Steinfeld J I J. Chem. Phys. 76 2201 (1982)
- 201. Schweitzer E L, Steinfeld J I Chem. Phys. 108 343 (1986)
- 202. Bertsev V V, Burtsev A P Opt. Spektrosk. **46** 199 (1979) [Opt. Spectrosc. (USSR) **49** 111 (1979)]
- Il'in S D, Selikhanovich V V, Gershenzon Yu M, Rozenshtein V B Khim. Fiz. 9 (9) 1192 (1990)
- 204. Gordienko V M, Dzhidzhoev M S, Panchenko V Ya, et al. Kvantovaya Elektron. (Mos cow) 9 2204 (1982) [Sov. J. Quantum Electron. 12 1432 (1982)]
- 205. Panchenko V Ya, Sizova I M, in *Matematicheskoe Modelir-ovanie Fizicheskikh Protsessov* (Mathematical Simulation of Physical Processes) (Eds V A Bushueva, V Ya Panchenko, O Yu Tikhomirov) (Moscow: Moscow State University, 1982) p. 72
- 206. Ivanov S V, Panchenko V Ya, Sukhorukov A P Vestn. Mosk. Univ. Ser. 3 Fiz. Astron. 25 (2) 64 (1984) [Mos cow Univ. Phys. Bull. 39 (2) 74 (1984)]
- 207. Ivanov S V, Panchenko V Ya, Sukhorukov A P Izv. Aka d. Nauk SS SR Ser. Fiz. 48 600 (1984) [Bull. Acad. Sci. USS R Phys. Ser. 48 185 (1984)]
- Dzhidzoev M S, Ivanov S V, Panchenko V Ya, Chugunov A V "Vibrational-rotational absorption saturation in small mole- cules" (Preprint No. 21) (Moscow: Physics Department of Moscow State University, 1984) p. 5

- Dzhidzhoev M S, Popov V K, Platonenko V T, Chugunov A V Kvantovaya Elektron. (Moscow) 11 1357 (1984) [Sov. J. Quantum Electron. 14 917 (1984)]
- Dzhidzhoev M S, Chugunov A V Vestn. Mosk. Univ. Ser. 3 Fiz. Astron. 26 (5) 49 (1985) [Moscow Univ. Phys. Bull. 40 (5) 61 (1985)]
- Dzhidzhoev M S, Platonenko V T, Chugunov A V Kvantovaya Elektron. (Moscow) 12 2200 (1985) [Sov. J. Quantum Electron. 15 1451 (1985)]
- 212. Chugunov A V, Djidjoev M S, Ivanov S V, Panchenko V Ya Opt. Lett. 10 615 (1985)
- 213. Ivanov S V, Panchenko V Ya, Chugunov A V *Izv. Akad. Nauk* SS SR Ser. Fiz. 50 695 (1986) [Bull. Acad. Sci. USSR Phys. Ser. 50 (4) 64 (1986)]
- Dzhidzhoev M S, Ivanov S V, Panchenko V Ya, Chugunov A V Kvantovaya Elektron. (Mos cow) 13 740 (1986) [Sov. J. Quantum Electron. 16 481 (1986)]
- 215. Ivanov S V, Panchenko V Ya, Sukhorukov A P Vestn. Mosk. Univ. Ser. 3 Fiz. Astron. 28 (1) 34 (1987) [Mos cow Univ. Phys. Bull. 42 (1) 37 (1987)]
- 216. Ivanov S V, Panchenko V Ya Kvantovaya Elektron. (Moscow)
 14 210 (1987) [Sov. J. Quantum Electron. 17 126 (1987)]
- Dzhidzhoev M S, Ivanov S V, Chugunov A V *Izv. Ak ad. Nauk* SS SR Ser. Fiz. **51** 254 (1987) [Bull. Acad. Sci. USSR Phys. Ser. **51** 42 (1987)]
- Chugunov A V, Ivanov S V, Panchenko V Ya Spectrochim. Acta Part A 43 171 (1987)
- 219. Ivanov S V, Panchenko V Ya Opt. Atm os. 2 (1) 55 (1989) [Atm os. Opt. 2 (12) 1081 (1989)]
- 220. Ivanov SV, Panchenko V Ya Khim. Fiz. 8 (4) 446 (1989)
- 221. Ivanov S V, Panchenko V Ya Opt. Atm os. 3 (1) 12 (1990)
- 222. Ivanov S V, Panchenko V Ya, in Itogi Nauki i Tekhniki Ser. Sovremennye Problemy Lazernoi Fiziki T. 1 Lazernaya Atomno-Molekulyarnaya Tekhnologiya i Diagnostika Elementarnykh Protsessov (Advances in Science and Technology, Series on Current Problems of Laser Physics, V. 1, Laser Atomic-Molecular Technology and Diagnostics of Elementary Processes) (Moscow: VINITI, 1990) pp 56-151
- 223. Raffel B, Wolfrum J Laser Chem. 10 (4) 207 (1990)
- 224. Raffel B, Warnatz J, Wolfrum J Appl. Phys. B 37 189 (1985)
- 225. Mordkovich N Yu, Lunin B S, Timofeev V V, Zhitnev Yu N Khim. Fiz. 7 (3) 382 (1988)
- 226. Lunin B S, Timofeev V V, Zhitnev Yu N Vestn. Mosk. Univ. Ser. 2 Khimiya 27 (2) 166 (1986)
- 227. Lunin B S, Kuricheva O V, Zhitnev Yu N Zh. Fiz. Khim. 60 2050 (1986)
- 228. Mordkovich N Yu, Lunin B S, Timofeev V V, Zhitnev Yu N *Khim. Fiz.* **6** (4) 455 (1987)
- 229. Zhitnev Yu N, Tveritinova E A, Shishnyaev V I Vestn. Mosk. Univ. Ser. 2 Khimiya 28 (4) 351 (1987)
- 230. Kaldor A, Braun W, Kurylo M J J. Chem. Phys. 61 2496 (1974)
- 231. Kaldor A, Braun W, Kurylo M J IEEE J. Quantum Electron. QE-11 697 (1975)
- 232. Gershenzon Yu M, Chekin S K Kinet. Katal. 18 1374 (1977)
- 233. West G A, Weston R E, Flynn G W Chem. Phys. Lett. 56 429 (1978)
- 234. Chekin S K, Gershenzon Yu M, Konoplyov A V, Rozenshtein V B Chem. Phys. Lett. 68 386 (1979)
- 235. Hänsel K D, in *Laser-Induced Processes in Molecules* (Berlin: Springer, 1979) p. 145
- 236. Quack M, Sutcliffe E Chem. Phys. Lett. 99 167 (1983)
- 237. Quack M, Sutcliffe E Chem. Phys. Lett. 105 147 (1984)
- 238. Quack M, Sutcliffe E Isr. J. Chem. 24 204 (1984)
- 239. Quack M, Sutcliffe E Chem. Phys. Lett. 121 315 (1985)
- 240. Bykov A D, Makushkin Yu S, Ulenikov O N Kolebatel'no-Vrashchatel'naya Spektroskopiya Vodyanogo Para (Vibrational-Rotational Spectroscopy of Water Vapour) (Novosibirsk: Nauka, 1989)
- 241. Gordienko V M, Biglow Z A, Danilov E O, et al., in Mode-Locked and Solid State Lasers, Amplifiers, and Applications (Eds M Pich, P W Pace) in Proc. SPIE Int. Soc. Opt. Eng. 2041 193 (1993)

- 242. Valentini J J, Moore D S, Bomse D S Chem. Phys. Lett. 83 217 (1981)
- 243. Valentini J J, Gerrity D P, Phillips D L, et al. J Chem. Phys. 86 6745 (1987)
- 244. Warnatz J Ber. Bunsen-Ges. Phys. Chem. 82 193 (1978)
- 245. Green S J. Chem. Phys. 92 4679 (1990)
- 246. Gelb A J. Phys. Chem. 89 4189 (1985)
- Aleksandrov E L, Sedunov Yu S Chelovek i Stratosfernyi Ozon (Man and Stratospheric Ozone) (Leningrad: Gidrometeoizdat, 1979)
- Grobecker A J "The CIAP report of findings: the effect of stratospheric pollution by aircraft", in *Proceedings of Fourth Conference CIAP*, *February 1975* pp 1–23
- 249. World Plan of Action on the Ozone Layer: UNE P Meeting of Experts, Washington DC, March, 1977
- 250. The Stratosphere 1981. Theory and Measurements. World Meteorological Office Global Ozone Research and Monitoring Project. Rep. No. 11 (Geneva: World Meteorological Organisation, 1982)
- 251. Atm ospheric Ozone 1985. Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change. Vol. 1–3 Global Ozone Research and Monitoring Project Report No. 16 (Geneva: World Meteorological Organization, 1986) 1095 pp
- Farman J C, Gardiner B G, Shanklin J D Nature (London) 315 207 (1985)
- Flaud J-M, Camy-Peyret C, Malathy Devi V, et al. J. Mol. Spectrosc. 124 209 (1987)
- 254. Yaroslavskaya E V, Skotnikov A I, Sverdlov L M "Solution of inverse and direct mechanical anharmonic spectroscopic problems for isotopes of $C_{2\nu}$ and C_s symmetry of the ozone molecule" Deposited Paper No. 948-82 (Moscow: VINITI, 1982)