Nonlinear laser spectroscopy of vibrational-rotational transitions in monoisotopic OsO_4 molecules and stabilization of CO_2 laser frequency

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The internal structure of Doppler-broadened absorption lines of the monoisotopic molecules $^{192}OsO_4$, $^{190}OsO_4$, $^{189}OsO_4$, and $^{187}OsO_4$ was observed experimentally and studied by a saturated-absorption laser spectroscopy technique using a CO_2 laser (10.6 μ). A quadrupole hyperfine structure is observed in the $^{189}OsO_4$ spectrum. The magnetic hyperfine structure of the $^{189}OsO_4$ and $^{187}OsO_4$ molecular spectra is considered. The feasibility and accuracy of the measurement of the energy of the nuclear isomer ^{189m}Os by means of a laser spectrometer are discussed. The narrow saturated-absorption resonances in the spectrum of OsO_4 with an even osmium isotope may be employed as frequency references to attain long-term frequency stability better than 10^{-13} in CO_2 lasers.

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1. INTRODUCTION

The development of methods of nonlinear laser spectroscopy without Doppler broadening (see, e.g., [1]) has made it possible to obtain information on very subtle details of vibration-rotation molecule spectra, details that could not be obtained by the methods of classical spectroscopy or even by methods of linear laser spectroscopy. A number of these effects was discussed earlier by one of the authors [2]. Foremost among them is the measurement of the hyperfine structure due to the quadrupole and magnetic interaction. The quadrupole interaction causes a splitting of the rotation-vibration lines by an amount 10^5-10^7 Hz that depends on the quadrupole-interaction constants and on the angular momentum of the molecule. The first experiments on the measurement of the quadrupole byperfine structure of infrared molecular transitions were carried out recently with the $^{12}CH_3{}^{35}Cl$ molecule. [3] The magnetic interaction between the angular momentum of the molecule and the spin of the nuclei causes a splitting by a much smaller amount, in the range 10^3-10^5 Hz. To observe the splitting it is necessary to have a resolution on the order of 10^9-10^{11}. The first successful experiments on the observation of the magnetic hyperfine structure in a vibration-rotation spectrum were carried out by Hall and Borde[4] with the aid of the $^{12}CH_4$ molecule. They obtained in their experiment an unprecedented nonlinear laser-spectroscope resolution on the order of 10^{10}.

Another effect that requires the use of nonlinear spectroscopy is the change in the structure of vibration-rotation transition following excitation of nuclei of a molecule to an isomeric state. In the isomeric state the nucleus usually has a spin that differs strongly from the spin of the ground state, and the mass of the nucleus increases by an amount $\Delta m = E_{exc}c^{-2}$. The isomeric shift in the vibration-rotation spectrum is of interest in that it makes it possible in principle to measure by methods of infrared molecular spectroscopy the excitation energy of metastable nuclei with high accuracy, regardless of the type of radioactive decay. We consider in this article the manifestation of all three effects in the vibration-rotation spectrum of monoisotopic OsO_4 molecules, namely the quadrupole, magnetic, and isomeric structure. To this end, we have investigated experimentally the internal structure of the Doppler-broadened absorption line of the monoisotopic molecules $^{187}OsO_4$, $^{189}OsO_4$, $^{190}OsO_4$, and $^{192}OsO_4$ with the aid of the series of lines of the P and R branches of the CO_2 laser. We observed experimentally the quadrupole structure in the spectrum of the $^{189}OsO_4$ and estimated the quadrupole-interaction constant, we also considered the magnetic hyperfine structure of the spectra of the molecules $^{187}OsO_4$ and $^{189}OsO_4$. The possibility of obtaining extremely narrow resonances and the choice of resonances for use as an exact natural frequency reference are analyzed. Preliminary results are presented of the stabilization of a CO_2 laser with external nonlinearly-absorbing cell in $^{192}OsO_4$. On the basis of the experiments and calculations, we discuss the possibility of measuring the energy of the nuclear isomer $^{189}OsO_4$ with a nonlinear laser spectrometer.

2. SPECTROSCOPIC DATA ON THE OsO_4 MOLECULE

The OsO_4 molecule has a high-symmetry structure [6] with the osmium atom at the center of a regular tetrahedron with four oxygen atoms at its corners, which are separated by a distance 1.71 Å. The OsO_4 molecule in the ground state has a symmetry group T_d (spherical top) and exhibits four fundamental vibrations: a fully-symmetrical vibration $\nu_1(A_1)$ at 965 cm^{-1}, two deformation vibrations $\nu_2(E)$ and $\nu_4(F)$ at 333 and 329 cm^{-1}, respectively, and one antisymmetrical vibration $\nu_3(F_2)$ at 960 cm^{-1}. Those active in the infrared spectrum are the triply degenerate vibrations ν_3 and ν_4.

The Os nucleus participates in the antisymmetrical vibration ν_3, the frequency of which agrees well with the 10.6-μ CO_2 laser band. The absorption spectrum of the OsO_4 in this region should be complicated. The vibration-rotational interaction leads to a splitting of the J-th rotational level of the vibrational state $v(\nu_3) = 1$ into rotational sublevels that are close in frequency (< 0.01 cm^{-1}), the number of which is determined by the symmetry types of the tetrahedral rotation subgroup. An additional complication in the infrared absorption spectrum of OsO_4 is introduced by the rich isotopic com-

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position of the molecule and, established in [7], by absorption in the hot bands with excitation of compound vibrations. Because of all these factors, the vibration-rotation spectrum of OsO_4 is a continuous contour made up of a tremendous number of absorption lines that overlap as a result of the Doppler effect [8]. Although the individual vibrational-rotational transitions could be observed with the aid of nonlinear laser spectroscopy methods [9], there is still no exact idea of the OsO_4 transitions responsible for the absorption of the CO_2 laser radiation.

The data concerning the absorption of the CO_2 laser radiation at $\lambda = 10.6$ in vapor of osmium tetroxide were published in [9,10]. The weak-signal absorption coefficients in OsO_4, measured in the maximum at the frequencies P(8)–P(24) and R(8)–R(24) lines of a CO_2 laser, fluctuate between 10^{-2} and 0.2 cm^{-1} $Torr^{-1}$.

All these data were obtained using osmium-tetroxide vapor with natural isotope content. To investigate in detail the spectrum of the OsO_4 it is necessary to use monisotopic molecules, otherwise it is impossible to make sense of the chaos of the lines. In the present study we investigated the spectra of four monoisotopic molecules: $^{192}OsO_4$, $^{190}OsO_4$, $^{189}OsO_4$, and $^{187}OsO_4$. The monoisotopic osmium tetroxide was prepared by heating the metallic powder of the corresponding osmium isotope to high temperatures (~600°C) in a quartz tube in an oxygen atmosphere. The composition of the isotopes in certain physical characteristics of the Os nuclei are given in the table.

3. NONLINEAR NARROW RESONANCES IN MONOISOTOPIC OsO_4 MOLECULES

The investigation of the characteristics of the narrow resonances observed inside the Doppler line of vibration-rotation transitions of the ν_3 band of the OsO_4 [9] molecule was carried with the aid of a nonlinear laser spectrometer employing the method of opposing weak waves. The method is based on the modulation of the transmission of a weak laser trial wave that interacts with molecules whose absorption is varied periodically by a strong opposing wave with modulated intensity (for details see [1]). The experimental setup was mainly analogous to that used in [11] to investigate narrow nonlinear resonances in the spectrum of the SF_6 molecule. We used a sealed cooled CO_2 laser operating on a series of vibration-rotation transitions of the P and R branches in the 10.6 μ region, with output power ~1 W in each line. Within the limits of the Doppler line of an individual transition, the laser frequency was tuned by scanning with a sawtooth voltage the position of the resonator output mirror mounted on a high-sensitivity piezoceramic double plate.

A semitransparent Ge plate, mirrors, and a system of NaCl collimating lenses were used to resolve the CO_2 laser beam in an internal low-pressure cell with OsO_4 into two plane waves traveling opposite to each other.

Parameters of the osmium nuclei used in the experiments

Os isotope	Abundance in nature, %	Enrichment, %	Nuclear spin, I	μ_{nuc}, nuc. magneton	Q_{nuc}, cm^2	Os isotope	Abundance nature, %	Enrichment, %	Nuclear spin, I	μ_{nuc}, nuc. magneton	Q_{nuc}, cm^2
192	41.0	96.5	0	–	–	189	16.1	88.9	$^3/_2$	0.65004	$0.8 \cdot 10^{-24}$
190	26.4	94.3	0	–	—	187	1.64	99.57	$^1/_2$	0.06432	–

The length of the nonlinearly absorbing cell was L_{abs} = 250 cm, the diameter was 36 mm, and the diameter of the light beam in the case of a Gaussian intensity profile was 25 mm. The ratio of the intensities of the opposing waves was 6 : 1, and the intensity of the strong traveling wave saturating the absorption was modulated at the frequency Ω = 200 Hz. To eliminate the influence of the back lighting on the operation of the CO_2 laser, the trial beam was transmitted through a cell with OsO_4 at a small angle (1–2 mrad) to the opposing beam and after reflection from the semiconducting mirror it was registered with a sensitive photodetector. The photodetector signal was amplified by a narrow-band amplifier at the modulation frequency Ω and was fed through a synchronous detector to the automatic recorder.

Nonlinear narrow saturated-absorption resonances were observed in the spectra of all the investigated monoisotopic molecules. Their relative location on the Doppler contour of the vibration-rotation transitions of the CO_2 laser are shown in Figs. 1a–1d. The accuracy with which the position of the resonance was measured was 20% and was governed by the hysteresis and nonlinearity of the scanning piezoelectric transmitter. The heights of the peaks in the figure corres-

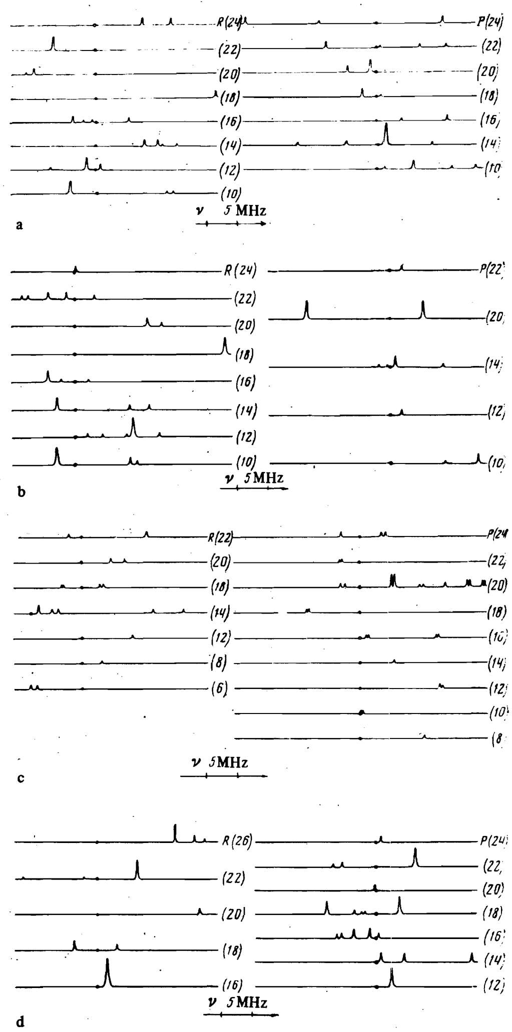

FIG. 1. Relative placements of the nonlinear narrow resonances in the spectrum of monoisotopic OsO_4 molecules on the Doppler-line emission contour for a number of CO_2-laser transitions: a, b, c, d—resonances in the spectra of the molecules $^{192}OsO_4$, $^{190}OsO_4$, $^{189}OsO_4$ and $^{187}OsO_4$, respectively.

ponds to the relative intensity of the narrow resonances of OsO_4.

The frequency region in which molecular resonances were observed extends from 940 to 954 cm^{-1} (the lines P(24)−P(8) of the CO_2 molecule and from 966 to 980 cm^{-1} (r(6)−R(26) lines of CO_2.) The structure of the spectra is due mainly to the lifting of the degeneracy with respect to the projection of the angular momentum J, as a result of the strong vibration-rotation interaction. A large contribution is also made to this structure by transitions connected with the excitation of weak compound vibrations. One cannot exclude the possibility that some of the resonances are due to the interaction of the laser light wave with two close transitions having a single common level [12].

The measurement of the absorption of infrared radiation in OsO_4 carried out by McDowell and Goldblatt[8] with a resolution 0.4 cm^{-1}, has made it possible to locate the center of the absorption band at 960.5 cm^{-1}. Using the approximate relation [13]

$$\nu_J = \nu_0 + 2B(1-G_3)J, \tag{1}$$

where $G_3 = 0.093$ is the Coriolis z-constant calculated from the value of the P−R interval for the ν_3 band, and $B = 0.1349$ cm^{-1} is the rotational constant for OsO_4, [8] we can find the corresponding quantum numbers J of the transitions on which the absorption of the laser radiation takes place. Absorption in OsO_4 in the 940−954 cm^{-1} band and in the 966−988 cm^{-1} band corresponds to transitions of the P and R branches, respectively, with values of J from 25 to 80. Differences in the isotopic composition of the molecules does not change this estimate, since the isotopic shift of the ν_3 vibration frequency amounts to approximately 0.26 cm^{-1} when the atomic mass of the osmium is changed by unity [8]

The transmission peaks of the trial wave were observed in the pressure range from 1 to 100 mTorr for all the monoisotopic molecules. The relative contrast of the most intense resonances reached 100%. The sensitivity of the observed nonlinear laser spectrometer with cross modulation of the absorption, determined by the relative amplitude of the weaker observable resonances, amounted to 3×10^{-3}% (at a signal/noise ratio = 1). The width of the narrowest resonances observed in the experiment was $\Delta\nu = 100 \pm 10$ kHz at a minimum OsO_4 pressure 8 mTorr.

We measured the absorption coefficient in monoisotopic OsO_4 molecules at the frequencies of several intense transmission resonances, and for this purpose the CO_2 frequency was tuned to their peaks:

Molecule:	$^{192}OsO_4$	$^{192}OsO_4$	$^{192}OsO_4$	$^{187}OsO_4$	$^{187}OsO_4$
CO_2-laser transition:	$P(14)$	$R(12)$	$R(14)$	$P(12)$	$R(16)$
κ_{Os}, $cm^{-1}Torr^{-1}$:	0.11	0.10	0,05	0,03	0,08

From an examination of the experimentally observed structure in the spectra of the four monoisotopic OsO_4 molecules we can note that as a rule one can observe on the contours of the CO_2-laser emission lines narrow resonances corresponding to simultaneous transitions of several monoisotopic molecules. Exceptions are the CO_2-laser R(6), R(8), and P(8) lines, on which absorption is observed only in $^{189}OsO_4$ vapor, and the R(26) line, at the frequency of which $^{187}OsO_4$ absorbs. In addition, there is predominant absorption by $^{192}OsO_4$ at the R(24) molecule and by the $^{187}OsO_4$ molecule at the lines P(12) and P(16) of the CO_2 laser. The total or preferred absorption of the radiation of the frequencies of the indicated CO_2 laser transitions by some monoisotopic OsO_4 molecule can used in a number of cases for selective excitation of the vibrations of the OsO_4 molecule with a definite osmium isotope, for example for laser separation of osmium isotopes, for the study of the processes of the transfer of vibrational excitation in the OsO_4 molecule, etc.

4. HYPERFINE STRUCTURE OF THE RESONANCES IN THE SPECTRUM OF THE MOLECULE $^{189}OsO_4$

The spectrum of the vibration-rotation transitions of the four investigated monoisotopic OsO_4 molecule has the following singularity: the spectrum of the $^{189}OsO_4$ molecule has the character of paired doublet resonances. This is most clearly manifest at the frequency of the P(20) line of the CO_2 laser (Fig. 2). The frequency difference between the doublet line fluctuates between 0.2 and 1 MHz, and as a rule is several times smaller than the frequency difference between the doublets. The rare single resonances in the $^{189}OsO_4$ spectrum can be attributed to admixtures of other monoisotopic molecules, mainly $^{190}OsO_4$ (6.4%), and also $^{182}OsO_4$ (2.2%) and $^{188}OsO_4$ (1.8%).

As seen from the table, the nucleus of ^{189}Os, unlike that of other isotopes, has a spin I = 3/2 in the ground state at relatively large magnetic and quadrupole moments. In the case of $^{192}OsO_4$ and $^{190}OsO_4$, owing to the fact that the spin of the nucleus is I = 0, there is no hyperfine splitting and individual resonances are observed in the spectrum. In the case of the $^{187}OsO_4$ molecule (I = 1/2), the absorption spectrum should be made more complicated by the magnetic hyperfine splitting. For the $^{189}OsO_4$ molecule (I = 3/2) it is necessary to take into account both the magnetic and the nuclear quadrupole interaction.

Let us consider the structure of the spectrum of the $^{189}OsO_4$ molecule in the case of quadrupole hyperfine splitting. The $^{189}OsO_4$ molecule pertains to the symmetry group T_d, i.e., it is a spherical top. Consequently, in the ground vibrational state the summary electric field produced by the molecular charges outside the nucleus at the site of the Os nucleus has spherical symmetry, and therefore there should be no hyperfine quadrupole splitting for it. In excited ν_3 vibrational states of the molecule, owing to the Coriolis interaction of both the jointly degenerate and different types of vibrations, the symmetry of the molecule is lowered, and the rotational sublevels of the excited vibrational states should be split by an amount [14]

$$W_Q = eq_J'Q[{}^3/_4C(C+1) - I(I+1)J(J+1)],$$

where (2)

$$q_J' = q_J/2I(2I-1)J(2J-1), \quad C = F(F+1) - I(I+1) - J(J+1);$$

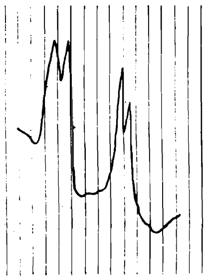

FIG. 2. Part of the experimental spectrum of the $^{180}OsO_4$ molecule at the frequency of the P(20) line of the CO_2 laser. One division = 500 kHz.

J, I, and F are the respective quantum numbers of the angular momentum of the molecule, the spin of the Os nucleus, and the total angular momentum of the system, while q_j is the average value of the second derivative of the potential produced by the charges outside the nucleus at the site of the nucleus along the **J** direction; Q is the quadrupole moment of the nucleus.

For the vibration-rotation transition v = 0 → v = 1, of the ν_3 vibration, the splitting scheme of the rotational sublevels and the expected spectrum are shown in Fig. 3. For the sake of argument we choose the transition at the frequency of the P(20) line of the CO_2 laser (10.6 μ), corresponding to an angular momentum J ≈ 65–70. The spectrum has the character of a doublet, each component of which is in turn split into two components. A more complicated spectrum structure should be observed in the case when the vibration-rotation transition takes place between two excited vibrational levels of the ν_3 band. In this case each of the levels of the transition (v, J → v′, J′) splits into four sublevels.

We calculate the energy of the allowed transitions ($\Delta F-0, \pm 1$), for the P, Q, and R branches of the vibrational transition v–v′ of the $^{189}OsO_4$ molecule and choose the most intense lines ($\Delta F = \Delta J$). In the expressions for the energies of the nuclear quadrupole interaction, written down for the cases of the P, Q, and R branches, we disregarded the dependence of q'_J on either the number v of the vibrational level or the value of J. As to the dependence of q'_J on v, it appears that it is quite weak for the transitions with Δv = ±1, [3], and the dependence of q'_J on J must be taken into account for the P and R branches only in the case of small J.

The calculated hyperfine structure of the vibration-rotation transition (v, J → v′, J′) of the ν_3 band of the $^{189}OsO_4$ molecule is shown in Fig. 4. In the actual calculation we assumed J equal to 50. As seen from Fig. 4, in the case of a transition between excited vibrational levels the qualitative structure of the most intense components of the nuclear quadrupole splitting for the P and R branches is likewise unchanged.

To explain finally the experimentally observed structure of the $^{189}OsO_4$ spectrum, let us examine the magnetic hyperfine splitting due to the nuclear spin of ^{189}Os. The energy of the magnetic hyperfine interaction is [14]

$$W_M = A\mathbf{JI} = A[F(F+1)-I(I+1)-J(J+1)], \tag{3}$$

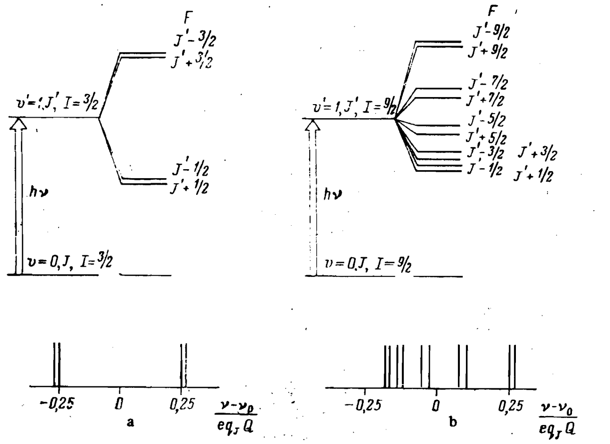

FIG. 3. Splitting of rotational sublevels of the transition v = 0 → v = 1 due to nuclear quadrupole interaction: a—for $^{189}OsO_4$, b—for $^{189m}OsO_4$.

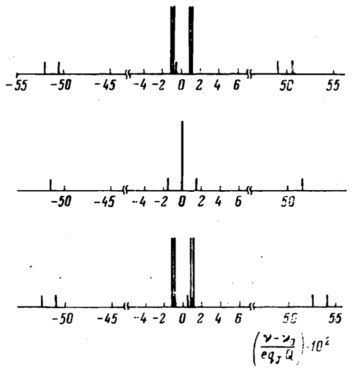

FIG. 4. Quadrupole splitting of the rotational sublevels of the transition v, J → v′, J′ of the ν_3 band of the $^{189}OsO_4$ molecule for the P, Q, and R branches (reading downward).

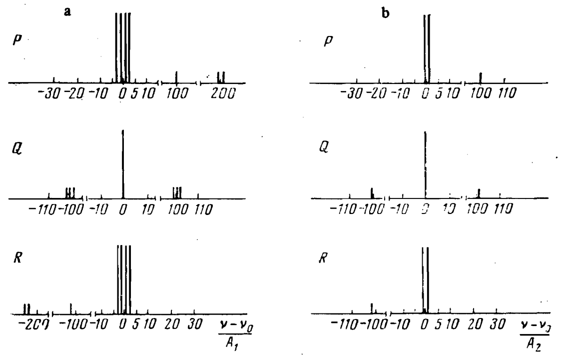

FIG. 5. Splitting of the rotational sublevels of the transition v(ν_3), J → v′(ν_3), J′ due to the nuclear magnetic interaction: a—for $^{189}OsO_4$, b—for $^{187}OsO_4$.

where A is the magnetic-coupling constant. A calculation of the energy of the most intense allowed transitions between the sublevels of the magnetic hyperfine structure ($\Delta F = \Delta J = 0, \pm 1$) was carried out for the general case of the P, Q, and R branches of the vibrational transition v–v′. Just as in the case of quadrupole splitting, it was assumed that $A_{v,J} = A_{v'J'}$ for all the branches of the transition. The calculated magnetic hyperfine structure of the vibrational-rotational transition (v, J → v′, J′) of the $^{189}OsO_4$ molecule is shown in Fig. 5a (the relative positions of the lines correspond to J = 50).

The most intense components of the spectrum for the $\Delta F = \Delta J = \pm 1$ transitions have the character of a tetraplet. From a comparison of the experimental (Fig. 1c) and calculated (Figs. 3a, 34, and 5a) spectra of the $^{189}OsO_4$ molecule we can make the definite conclusion that the observed doublet structure of the vibration-rotation transitions of the ν_3 band is due to nuclear quadrupole splitting. A more thorough analysis of the experimental results allows us to state that the pair resonances shown in Fig. 1c are the intense complicated doublets shown in Figs. 3a or 4, the components of which were not resolved experimentally. Favoring this explanation are also the following simple considerations: The quadrupole-interaction constant eq_JQ for the $^{189}OsO_4$ is unknown, but the known data for a number of heavy five-atom molecules [14] allow us to assume that its value for $^{189}OsO_4$ does not exceed several MHz. With this estimate, the maximum value of the splitting between the separated doublets of the transitions (v = 0 → v′ = 1, J ~ 65–70) will be of the order of 1 MHz (an experimentally observable splitting), and the frequency difference between the components of the doublets is 10^{-2} MHz, which is smaller by one order of magnitude than the resolution of the employed laser spectrometer.

The quadrupole-interaction constant eq_JQ calculated for $^{189}OsO_4$ from the experimentally observed (Fig. 1c) nuclear quadrupole splitting of the vibration-rotation transition v = 0 → v = 1 of the ν_3 band at the P(20)-line frequency of the CO_2 laser (the most intense doublets) amounts to 0.6 MHz (within the accuracy to which J^2 is determined), while $q_J = 3 \times 10^{15}$ V/cm^2.

The energy of the magnetic hyperfine splitting for the $^{189}OsO_4$ molecule, as for most polyatomic molecules with an even number of electrons, is much smaller than the energy of the nuclear quadrupole splitting [14]. Therefore the magnetic hyperfine structure of the spectrum was not observed in this study, and its resolution lies beyond the limits of the resolution of the employed laser spectrometer. The same pertains also to the magnetic hyperfine structure of the spectrum of $^{187}OsO_4$. Although allowance for the magnetic moment of ^{187}Os leads to the appearance of doublets in the spectrum (Fig. 5b), in our experiments we observed only individual narrow resonances of $^{187}OsO_4$ on the contours of the CO_2-laser emission lines.

5. BROADENING OF NARROW RESONANCES BY A FIELD AND UNDER PRESSURE

A detailed investigation of the behavior of narrow OsO_4 resonances in a radiation field and under pressure was carried out at the frequency of the P(14) line of the CO_2 laser, at which the largest absorption was observed in $^{192}OsO_4$, and the most intense and contrasting resonance is observed near the center of the laser gain line. The resonance corresponds to a vibration-rotation transition in the $^{192}OsO_4$ spectrum with angular momentum J on the order of 45.

We investigated the broadening of narrow resonance on the intensity of the radiation field and as a result of the pressure in the region of low pressures of $^{192}OsO_4$, when the absorption line is inhomogeneously broadened. To this end we measured in the experiments the absorption saturation parameter for the indicated transition. The procedure of determining this parameter did not differ from that first described in [26] for an investigation of the characteristics of narrow resonances in the spectrum of sulfur hexafluoride. In the traveling-wave regime, we measured the transmission of the wave as a function of the level of its intensity at the entrance of a nonlinearly absorbing cell with $^{192}OsO_4$ for different values of the optical density of the cell $d = \kappa_0 L$ (Fig. 6). Inasmuch as we used sufficiently dense cells (d = 0.24–1.54), it was necessary, when determining the saturation parameter, to take into account the attenuation of the wave on passing through the absorbing cell. In [26] this was taken into account and a calculated plot was obtained for the transmission of a plane traveling wave through the cell at various optical densities d as a function of the field intensity (in units of I/I_S). The corresponding values of the saturation parameter I_S were obtained by making the experimental curves (Fig. 6) coincide with the calculated ones at the same value of d.

Within the pressure range from 8 to 57 mTorr, the dependence of the intensity of absorption saturation on the pressure of $^{192}OsO_4$ has a linear character:

$$I_s = 0.1p \text{ mW-mTorr}^{-1}\text{ cm}^{-2}$$

A similar dependence can be obtained also by another method, if one knows from experiment the resonance broadening by a strong field (Fig. 7) and one uses the calculated dependence of the transmission-resonance widths on the field [11]:

$$\Delta\nu = \Delta\nu_0 + \Gamma\left(\sqrt{1+I_1/I_s} + \sqrt{1+I_2/I_s}\right). \quad (4)$$

Here Γ is the homogeneous half-width of the line, I_1 and I_2 are respectively the intensities of the strong forward and weak backward wave, $\Delta\nu_0$ is the limiting resolution of the nonlinear laser spectrometer. The latter is made up mainly of the broadening due to the fact that the opposing waves are not parallel (~50–60 kHz) and of the broadening due to the finite time of flight of the molecule through the light beam. The results obtained in both cases were in agreement.

The absorption-saturation intensity measured for OsO_4 vapor with natural Os isotope content turned also to be a linear function of the pressure in this range of pressures, with a slope 0.27 ± 0.05 mW-mTorr^{-1}cm^{-2}. This last result differs from the data of Bazarov, Gerasimov, and Posudin[10] (I_S = 0.8 W-Torr^{-1}cm^{-2}). We attribute this discrepancy to the fact that the measurements of [10] of the absorption-saturation intensity in OsO_4 did not take into account the effects of thermal population of the vibrational level of the molecules, which begin to play a significant role at OsO_4 pressures above 0.1 Torr.[7]

By approximating the curves shown in Fig. 7 in the weak-field region ($I_1, I_2 \ll I_S$) we obtain the dependence of the transmission resonance widths Δν on the $^{192}OsO_4$ pressure in a nonlinearly absorbing cell. The associated homogeneous width 2Γ of the transition for the $^{192}OsO_4$ molecule varies linearly with the pressure, with a pro-

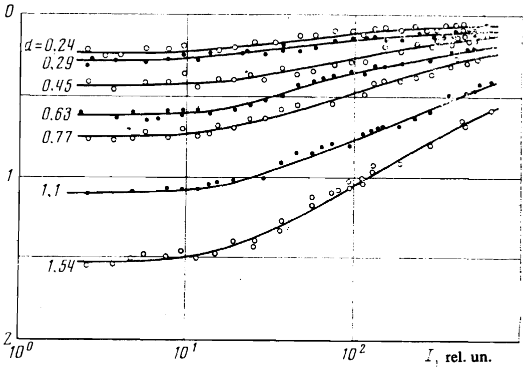

FIG. 6. Transmission of traveling wave $\ln(I_{in}/I_{out})$ vs. its intensity at the entrance into a cell with $^{192}OsO_4$ at different initial optical cell densities $d = \kappa_0 L$.

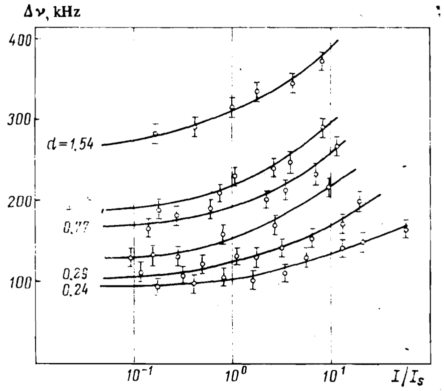

FIG. 7. Width Δν of the transmission peak as a function of the degree of saturation of the absorption of the strong wave at the entrance to the cell with $^{192}OsO_4$ for different values of d (reading downward): 1.54, 1.1, 0.77, 0.63, 0.29, and 0.24.

portionality coefficient 3.7 ± 0.4 MHz/Torr (Fig. 8). In the Lorentz-broadening model, the time of the transverse relaxation due to the collisions between the molecules is given by $pT_2 = 8.6 \times 10^7$ sec-Torr, and the molecule mean free path relative to the broadening collisions is $pl_{\text{trial}} \approx 1.5$ cm-Torr.

6. CHOICE OF RESONANCES FOR THE STABILIZATION OF A CO_2 LASER

The narrow resonances observed within the Doppler-broadened lines of the vibration-rotation spectrum of monoisotopic OsO_4 lines can be used to stabilize the frequency of a CO_2 laser. As is well known, the criteria for the choice of molecular resonances as references for the stabilization of a laser frequency of the absence of a hyperfine structure, a sufficiently large absorption coefficient at the transition frequency, and proximity of the transition frequency to the center of the laser gain line. All these conditions, of course, are necessary only to obtain extremely narrow and frequency-stabilized resonances. The automatic frequency control of a laser at the peaks of these lines makes it possible in this case to obtain maximum long-term stability and reproducibility of the frequency. If ultrahigh laser frequency stability is not required by the particular task, then in principle any of the observable (Fig. 1) nonlinear narrow resonances of the monoisotopic molecules OsO_4 can be used to stabilize the frequency of a CO_2 laser. It is of course more convenient, however, to work with intense single resonances near the center of the gain line on such laser transitions as P(14), P(20), R(10), R(12), and R(22) with the $^{192}OsO_4$ molecule, on the transitions P(20), R(10), and R(14) with the $^{190}OsO_4$ molecule, on the transition P(20) with the $^{189}OsO_4$ molecule, and on the transitions P(12), P(18), P(22), R(16), and R(22) with the $^{187}OsO_4$ molecule.

To obtain extremely exact molecular frequency standards we can use monoisotopic OsO_4 molecules with only even osmium isotopes (spin I = 0). Of practical value are the molecules with the even osmium isotopes having the largest natural abundance, namely

$$^{192}Os\ (41.0\%),\quad ^{190}Os\ (26.4\%)\quad ^{188}Os\ (13.3\%).$$

The absence of nuclear hyperfine splitting makes these molecules in conjunction with the CO_2 laser good competitors of methane, the P(7) transition of the ν_3 band of which is used to stabilize the He-Ne laser frequency at λ = 3.39 μ with a record accuracy for the IR band, namely 10^{-4}.[15] As observed by Hall and Borde[4], the P(7) transition of the ν_3 band of the CH_4 molecule has a structure governed by the spin-rotational interaction in the molecule and by the spin-spin interaction between the protons. A similar structure will apparently be possessed also by the vibrational-rotational transitions of the ν_3 band of the SF_6 molecule (a long-term frequency stability on the order $10^{-12}-10^{-13}$ was attained with this molecule, the highest value for CO_2 lasers [16,17]), although the spin-rotation and spin-spin interactions in this molecule (the spin of the fluorine nucleus 1/2) are much weaker than in methane. An additional advantage of the OsO_4 molecule as a frequency standard is the exclusively low value of the splitting of the narrow resonance, Δ ~ 20 Hz, due to recoil effects in the emission (absorption) of a vibrational quantum by the molecule.[18]

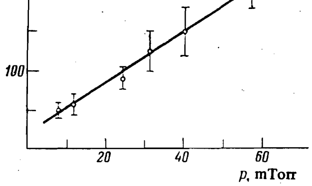

FIG. 8. Homogeneous transmission width 2Γ as a function of the $^{192}OsO_4$ pressure.

The OsO_4 molecules have an absorption coefficient on the order of 10^{-1} cm^{-}Torr for a number of transitions in the 10.6 μ region. This is sufficient to work at very low vapor pressures ~10^{-4} Torr and to obtain extremely narrow resonances. Indeed, the average thermal velocity of the OsO_4 molecule at T = 300° K is equal to

$$v_0=\sqrt{8kT/\pi M}=1.7\cdot 10^4\ \text{cm/sec}$$

At a light-beam diameter d = 2.5 cm at half-height, with a Gaussian profile of the intensity, the width of the resonance due to the finite time of interaction of the field with the molecule is

$$\Delta\nu_{\text{transit}} \approx \frac{1}{2\pi}\frac{v_0}{d} \approx 1\ \text{kHz}$$

(of the order of the broadening due to diffraction). When such narrow resonances are obtained, the resolution of the nonlinear laser spectrometer can be improved to 3×10^{-11}. At the present status of the automatic frequency control techniques, the accuracy $\Delta\nu/\nu$ at which a laser frequency can be maintained at the peak of a narrow resonance is better than 3×10^{-14}. In addition to decreasing the relative width of the reference line, the decrease of the pressure of the molecular gas could lead to an appreciable decrease of the collision shift of the frequency [15] of the absorbing vibration-rotation transition in OsO_4, and consequently should make possible high reproducibility of the CO_2-laser frequency.

In our study the CO_2-laser frequency was stabilized with a servomechanism system against the peak of the narrow resonance of $^{192}OsO_4$ on the contour of the P(14) line. The frequency was stabilized by the standard automatic frequency control method against the zero of the first derivative of the frequency reference.

The laser frequency oscillated sinusoidally near the center of a narrow peak because of the weak sinusoidal modulation of the resonator length at acoustic frequency f. The radiation passed through an external nonlinearly-absorbing cell (L = 250 cm), and a small fraction (~10%) of the radiation passing through the cell was reflected at a small angle in the backward direction and was registered, after passing again through the cell, by a photodetector. In the experiment, the pressure of the $^{182}OsO_4$ vapor in the cell was 15 mTorr, and the width of the transmission peak of the weakly-reflected wave was 250 ± 30 kHz. The error signal generated by the servo system at the frequency f was amplified and fed with the proper phase, to a piezoelectric element that controlled the laser frequency. To decrease the weak distortion of the discrimination curve, due to the approximate difference of 1.5 MHz between the centers of the gain and absorption lines, the laser radiation was first passed through a short attenuator cell with SF_6 : He, which smoothed out the dependence of the output power on the frequency within the limits of the narrow resonance.

The CO_2 laser had an assured free-running frequency stability 10^{-10} over 1 msec.[16] The servo-system stabilization coefficient K amounted to 30 000, and the transmission bandwidth for the system used to eliminate the frequency perturbations was ~16 Hz. The relative frequency stability of the CO_2 lasers was determined from the difference frequency of the radiation of two independently stabilized lasers, measured with the aid of an electronic-computing frequency meter. The calculated frequency difference was recorded with a special converter on magnetic tape, and was then reduced with a computer. This converter and recording block were developed at the Earth Physics Institute of the USSR Academy of Sciences. The results of experiments performed under ordinary laboratory conditions were obtained in the form of the Allan parameter [19].

The relative long-term stability of the CO_2 laser with an external cell with $^{192}OsO_4$, obtained in the first experiments, was 3×10^{-12} at an average time of 100 sec. Naturally, this frequency stability is not the limit and characterizes only the available experimental setup. We did not measure the frequency reproducibility of lasers with an absorbing $^{192}OsO_4$ cell.

7. ISOMERIC STRUCTURE OF VIBRATIONAL-ROTATIONAL TRANSITION IN THE SPECTRUM OF $^{189}OsO_4$

The OsO_4 molecule is also of interest for the investigation of the isomeric structure and the isomeric shift of vibrational-rotational transitions in the excitation of metastable states of the Os nucleus.

There are several isomeric Os nuclei [20]. An optimal candidate from the point of view of the half-life and abundance of the isotope in nature, for measurements of the isomeric structure and the shift, is the isomer ^{189m}Os. It is produced from iridium obtained in the reaction $^{188}Os(d, n)$,[21] and γ-decays to the ground state with $\Delta E_\gamma = 30.8$ keV.

The increase of the internal energy of the Os nucleus is equivalent to the Einstein change of the nuclear mass $\Delta m = c^{-2}\Delta E$, and consequently should lead to a change in the frequency of the vibrational-rotational transitions of the ν_3 band observed in the OsO_4 spectrum with the unexcited Os nucleus. This change depends on the nuclear excitation energy ΔE and is determined by the symmetry and by the quantum state of the molecule.

On the other hand, when the Os nucleus is excited, a simultaneous change takes place in the hyperfine structure of the spectrum, because the isomeric states of the nuclei differ from the ground state by the value of the nuclear spin. In the case of the ^{189m}Os isomer the spin of the nucleus is $I = 9/2$. The infrared absorption spectrum of the $^{189m}OsO_4$, just as in the case of the ground state of the ^{189}Os nucleus ($I = 3/2$), is an aggregate of vibration-rotational transition hyperfine components due to nuclear quadrupole splitting. The expected spectrum for $^{189m}OsO_4$ corresponding to the simplest case of absorption of laser radiation on the transition $v(\nu_3) = 0, J \rightarrow v(\nu_3) = 1, J'$ is shown in Fig. 3b (for convenience in the comparison of the spectra, we consider the transition at the frequency of the P(20) line of a CO_2 laser, with J ~ 65 to 70). It is seen from the figure that the change of the internal structure of the vibrational-rotational transition in the $^{189m}OsO_4$ spectrum does not exceed the quadrupole splitting of the transition in the spectrum of the $^{189}OsO_4$ molecule with unexcited Os nucleus. Just as for $^{189}OsO_4$ it is possible to calculate for the $^{189m}OsO_4$ molecule in the more general case, when both vibrational states of the molecule are excited.

The isomeric shift of the frequency ν_3 can be obtained, for example, by measuring the difference frequency of CO_2 lasers independently stabilized against the vertices of narrow resonances of the $^{189}OsO_4$ molecule with excited and unexcited Os nuclei, respectively.

Of course, in both cases the spectrum of the vibration-rotational transitions of the molecule should be identified beforehand and the transitions with identical values of the quantum numbers v, J, and K must be indicated. The transitions can be identified on the basis of the theory developed in [22–24] for a spherical-top type molecule.

To calculate the isomeric frequency shift $\Delta\nu_3^m$, let us consider a contribution of Δm to the vibrations and the rotation of the molecule. In the case, for example, of a diatomic molecule AB, excitation of the nucleus of atom A changes the oscillation frequency ν_0 by an amount

$$\Delta\nu^m = -\frac{\Delta E}{2c^2}\frac{M_B}{M_A(M_A+M_B)}\nu_0, \qquad (5)$$

where M_A and M_B are the masses of the atoms with unexcited nuclei. In the calculation of the isomeric shift $\Delta\nu_3^m$ for a polyatomic molecule with symmetry T_d it is necessary to take into account the connection between the ν_3 vibration and the ν_4 vibration (both vibrational modes belong to the same symmetry type F_2), and also the strong coupling of the vibrations of the nuclei with the rotation of the molecule. We recall that in the OsO_4 molecules, at angular momentum values J ~ 25–80, the spherical symmetry of the molecule is distorted not only by the Coriolis-interaction forces, but also as a result of the large centrifugal forces acting in the molecule. Unfortunately, for these reasons no exact calculation of the isomeric shift of the vibrational transitions in OsO_4 absorbing CO_2-laser radiation can be carried out at present, since it calls for knowledge of the force constants and the interaction constants in the molecule with an accuracy that is as yet unattainable.

In the rigid-oscillator approximation, the isomeric shift of the frequency ν_3 of the $^{189m}OsO_4$ molecule can be estimated by starting from the isosopic frequency shift of the center of the ν_3 band when the mass of the Os nucleus is changed by one atomic mass unit. The latter was calculated by McDowell and Goldblatt[8] on the basis of the Redlich-Teller rule for isotopic frequencies and known force constants of the OsO_4 molecule. Its value $\Delta\nu_3^i$ is ~ 0.26 cm^{-1}. The corresponding isomeric shift of the transition $v(\nu_3) = 0 \rightarrow v(\nu_3) = 1$ (J, $\Delta J = 0$) in the $^{189m}OsO_4$ molecule is $\Delta\nu_3^m = \Delta m \Delta\nu_3^i \approx 264$ kHz (Δm is given here in atomic mass units), i.e., it lies within the resolution limit of the nonlinear laser spectrometer. Allowance for rotation of the molecule introduces a correction of this quantity, but can hardly change the estimate.

Thus, the isomeric shift and the isomeric structure of the vibrational-rotational transitions of the $^{189m}OsO_4$ molecule can be qualitatively observed by methods of nonlinear laser spectroscopy, but it appears that they cannot be connected with the excitation energy of the ^{189m}Os nucleus with accuracy better than 0.1%. This conclusion pertains also to other polyatomic molecules characterized by a coupling between the vibrations and by absorption of the radiation in transitions with large angular momentum **J**. For an exact measurement of the energy of the excited metastable states of nuclei it is preferable to carry out, with the aid of a frequency-tunable laser, nonlinear spectroscopy of diatomic molecules with an isomeric nucleus that have a sufficiently high excitation energy (>1 MeV).

We note that it will apparently be difficult to obtain narrow resonances of saturated absorption in the spectrum of molecules with radioactive nuclei because of the insufficiently high radioactivity of the cell with the absorbing gas. For example, for the $^{189m}OsO_4$ molecule ($T_{1/2} = 5.7$ hr) at a pressure 10^{-4} Torr, and a cell diameter 10 cm and length 2.5 m, the radioactivity of the gas amounts to $\sim 10^2$ Ci. It becomes therefore necessary to develop new methods for registering nonlinear narrow resonances within the Doppler line, with small amounts of ^{189m}Os in the absorbing cell. One such method is registration of the resonances of the density of the excited molecules with the aid of ultraviolet absorption from their vibrational levels [25].

8. CONCLUSION

We used the methods of nonlinear laser spectroscopy within the Doppler line to observe the quadrupole structure of vibration-rotation transitions of the ν_3 band of the $^{189}OsO_4$ molecule. We have demonstrated the possibility of increasing the resolution of a nonlinear spectroscope based on a CO_2 laser, to a level 10^{10}, to permit a complete investigation of the quadrupole and magnetic hyperfine structures of the monoisotopic OsO_4 molecules.

The vibration-rotation transitions of monoisotopic OsO_4 molecules with even Os isotopes can be used as high-accuracy references for the stabilization of a CO_2 laser frequency. The most suitable for this purpose are the intense narrow resonances observed on the contours of a number of CO_2-laser lines near the center: P(14), P(20), R(10), R(12), and R(22) for $^{192}OsO_4$ and P(20), R(10), and R(14) for $^{190}OsO_4$. This uncovers a possibility of obtaining long-term frequency stability better than 10^{-13} for CO_2 lasers by using an external nonlinearly-absorbing OsO_4 cell.

We have demonstrated the possibility and ways of employing nonlinear laser spectroscopy for a qualitative observation of the isomeric structure and frequency shift in vibrational-rotational spectrum of the OsO_4 molecule with isomeric nuclei of osmium, and of measuring the isomer energy.

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