

# Direct observation of the nonequilibrium excitation of high vibrational levels of the $\text{OsO}_4$ molecule by a high-power laser pulse, and separation of osmium isotopes

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Nonequilibrium population of the vibrational levels  $v \geq 10$  was revealed by the change of the vibrational structure of the UV spectrum following the action of a high-power  $\text{CO}_2$  laser pulse on the  $\text{OsO}_4$  molecule. A 15% enrichment of the osmium isotopes was obtained from the action of a strong IR field.

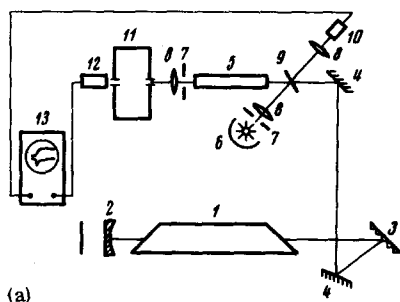
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1. Observation of isotopically-selective dissociation of molecules in multiquantum absorption in a strong IR field<sup>[1,2]</sup> has raised the question of the kinetics of the behavior of polyatomic molecules in a strong IR field, and the possibility of using this method for isotope separation.

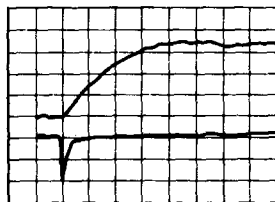
We report here for the first time the direct observation of highly-excited vibrational levels (with energy  $> 1$  eV) induced by a pulse of IR radiation, and also the separation of the isotopes of the heavy element Os ( $A = 190.2$ ) in the  $\text{OsO}_4$  molecule, in which the isotopic shift per unit mass ( $\Delta\nu \approx 0.26 \text{ cm}^{-1}$  for the  $\nu_3$  vibration<sup>[3]</sup>) is much less than the width of the absorption band (the half-width of the Q branch is  $3-4 \text{ cm}^{-1}$ ).

2. Vibrationally-excited states of the  $\text{OsO}_4$  molecule were observed on the  $3200 - 2700 \text{ \AA}$  transition  $\tilde{A} - \tilde{X}$ ,<sup>[4]</sup> in which there appears a fully-symmetrical  $\nu_1$  vibration ( $971 \text{ cm}^{-1}$ )<sup>[5]</sup> that is active only in the Raman scattering

spectrum. In the experiments, a high-power  $\text{CO}_2$ -laser pulse ( $\sim 10 \text{ MW/cm}^2$ ) excited the  $\nu_3$  vibration ( $960 \text{ cm}^{-1}$ ), and from the changes in the electron-vibrational spectrum we determined the population of the upper vibrational levels, the times and the character of the intramolecular V-V exchange, and also the parameters of the vibrational-translational and vibrational-rotational relaxation. The experimental setup is shown in Fig. 1. A  $\text{CO}_2$  atmospheric-pressure laser with selection of the rotational transitions radiated pulses of 3 J energy and duration 90 nsec at half-height. The radiation, in the form of an unfocused beam, was directed to a cell with  $\text{OsO}_4$  100 cm long and 30 mm in diameter. The excited gas was simultaneously illuminated by a source of visible radiation with a continuous spectrum, which was analyzed at the exit from the cell with a monochromator. The registration system had a time resolution not worse than 60 nsec. A monochromator was used to cut off spectrum sections corresponding to the transitions with  $v'' \geq 1$  of the  $\nu_1$  vibration of the ground electronic state  $\tilde{X}$  to the levels  $v' = 0$  of the excited state  $\tilde{A}$ ,



(a)



(b)

FIG. 1. a) Experimental setup: 1— $\text{CO}_2$  laser, 2—resonator mirror, 3—diffraction grating, 4—rotating mirrors, 5—cell with  $\text{OsO}_4$ , 6—IFP-800 flash lamp, 7—diaphragms, 8—lenses, 9— $\text{BaF}_2$  plate, 10—photon-drag detector, 11—MDR-2 monochromator, 12—FEU-39 photomultiplier, 13—S8-2 oscilloscope. b) Top-shape of typical signal of electron-absorption in  $\text{OsO}_4$ , induced by a laser pulse (sweep  $0.5 \mu\text{sec/div.}$ ,  $\text{OsO}_4$  pressure 0.4 Torr). Bottom—exciting laser pulse.

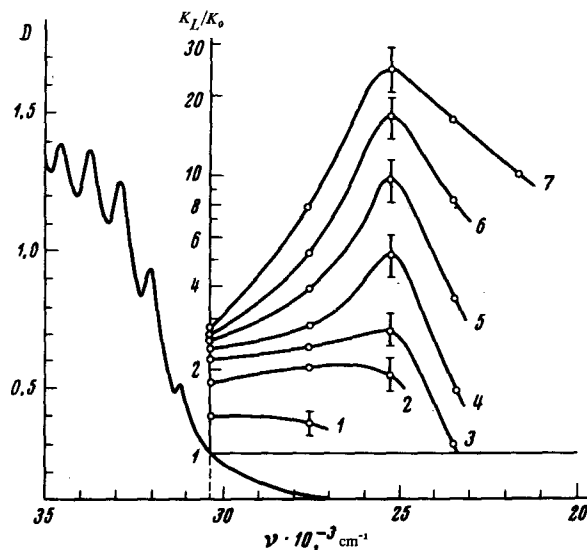


FIG. 2. Changes in the electron absorption spectrum of  $\text{OsO}_4$  at the exciting radiation intensities 2, 4, 6, 7, 8, 9, and 10  $\text{MW/cm}^2$  (1-7, respectively).  $K_L$  is the absorption coefficient in the case of laser excitation, and  $K_0$  is the coefficient without excitation. On the left side is shown the long-wave edge of the  $\text{OsO}_4$  electron absorption band ( $D$  is the optical density).

CO <sub>2</sub> -laser line	OsO <sub>4</sub> pressure, Torr	C <sub>2</sub> H <sub>4</sub> pressure, Torr	OCS pressure, Torr	<sup>192</sup> Os enrichment relative to <sup>187</sup> Os, %	<sup>187</sup> Os enrichment relative to <sup>192</sup> Os, %
R(2)	0.10	0.4	—	15.5 ± 4	—
R(2)	0.16	0.16	—	10 ± 3	—
R(2)	0.24	1.0	—	8 ± 3	—
R(2)	0.16	—	0,16	12 ± 4	—
P(2)	0.16	1.0	—	—	9 ± 3

and the time dependence of the electron absorption at these frequencies was analyzed.

3. The waveform of a typical electron absorption signal is shown in Fig. 1b. The character of the deformation of the electron absorption band  $\nu'$ ,  $\tilde{A} \rightarrow \nu''$ ,  $X$  is shown in Fig. 2. A shift is observed to the long-wave side of the edge of the absorption band. This shift depends strongly on the pulse intensity. The band deformation corresponds to nonequilibrium population of the upper vibrational levels, the population kinetics of which was investigated with the aid of the electron-absorption pulse waveform. For all the investigated transitions with different  $\nu''(\nu_1)$ , the shape of the electron-absorption pulse is the same, and there is no noticeable change of the spectrum during the time of the CO<sub>2</sub>-laser pump pulse. The reason is that the excited vibration is  $\nu_3$ , which does not appear in the electron spectrum, and the absorbed energy is concentrated in the  $\nu_3$  vibration. A change in the spectrum of the electronic transition is possible only following V-V exchange of excitation between the vibrations  $\nu_3-\nu_1$ ,  $\nu_2$ ,  $\nu_4$ . The independence of the shape of the pulse of the electron-absorption wavelength indicates that the levels populated immediately are the high-lying vibrational ones. The maximum measured shift of the red boundary of the absorption band was  $\Delta\nu_{\text{shift}} \approx 10^4 \text{ cm}^{-1}$ , thus indicating that the levels  $\nu''(\nu_1) = \Delta\nu_{\text{shift}}/\nu_{\text{laser}} \approx 10$  are populated after the V-V exchange. It follows therefore that the IR laser radiation populates the vibrational levels of the  $\nu_3$  vibration with energy several times larger than  $\hbar\omega\nu''(\nu_1) \approx 1 \text{ eV}$ .

4. The osmium isotope separation were separated by focusing ( $f=50 \text{ cm}$ ) a CO<sub>2</sub> laser beam into a stainless-steel cell 50 cm long and 12 mm in diameter. In the region of the focus we observed visible luminescence of the dissociation products. Since the dissociation produced by irradiating OsO<sub>4</sub> with infrared radiation from a CO<sub>2</sub> laser is reversible, an acceptor for the radical must be present in the reaction zone. The acceptors used were H<sub>2</sub>, NO, CO, C<sub>2</sub>H<sub>4</sub>, and OCS.

<sup>184</sup>Os (0.018%), <sup>186</sup>Os (1.592%), <sup>187</sup>Os (1.64%), <sup>188</sup>Os (13.3%), <sup>189</sup>Os (16.1%), <sup>190</sup>Os (26.4%), and <sup>192</sup>Os (41.0%). To increase the sensitivity of the registration of the enrichment, the OsO<sub>4</sub> was prepared in such a way that the concentrations of the <sup>187</sup>OsO<sub>4</sub> and <sup>192</sup>OsO<sub>4</sub> molecules, the isotopic shift between which amounts to  $\sim 1.3 \text{ cm}^{-1}$ , were practically the same. The ratio of the concentrations of these molecules prior to the irradiation was  $[\text{<sup>192</sup>OsO}_4]/[\text{<sup>187</sup>OsO}_4] = 1.18 \pm 0.02$ . The enrichment was determined during the registration of the mass spectra prior to the irradiation and after irradiating the cell with  $\sim 10^4$  pulses. Several typical results of these experiments are listed in the table.

It should be noted that the low enrichment coefficient can be attributed, in particular, to the low power levels at the P(2) and R(2) lines of the CO<sub>2</sub> laser emission ( $\sim 70 \text{ MW/cm}^2$  at the focus of the lens), whereas experiments on the separation of sulfur isotopes<sup>[2]</sup> have shown that the enrichment coefficient increases exponentially with increasing irradiation intensity.

5. Our results show that by multiquantum absorption in a strong IR field it is possible to separate isotopes of heavy elements with a small isotopic shift. The enrichment coefficient can be increased in this case by cooling the molecular gas, particularly by letting it escape from a nozzle into vacuum.<sup>[6]</sup> In addition, the observed rapid dissociation of the CCl<sub>4</sub> molecule following excitation of the compound vibration  $\nu_2 + \nu_3$  with a CO<sub>2</sub> laser demonstrates that this method can be used also to separate isotopes of elements in compounds for which the CO<sub>2</sub>-laser emission coincides with the frequency of an overtone or a combination vibration, such as MoF<sub>6</sub>, WF<sub>6</sub>, TiCl<sub>4</sub>, and others.

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