

Observation of inverse radiationless transitions when polyatomic molecules are excited by IR laser emission

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Collisionless transfer of vibrational energy to the electrons was observed in multiphoton absorption of IR laser emission by the OsO_4 molecule.

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1. We have observed, for the first time ever, *collisionless* excitation of electronic states of a polyatomic molecule by buildup of its vibrations in an IR laser field.¹ Since this phenomenon is due to the same nonadiabatic coupling of the electronic and nuclear motions which causes the well known radiationless transitions of electron energy into vibrational energy in polyatomic molecules,² we have named the observed process "inverse radiationless transition."

Multiphoton absorption of polyatomic molecules in an IR laser field makes it possible to excite high-lying vibrational states of these molecules and produce dissociation.¹ Since the nonadiabatic coupling of the electron and laser motions becomes significant for high-lying vibrational states (the Born-Oppenheimer approximation is violated), one can expect to observe, besides the dissociation via the electronic ground state in the presence of suitable excited electronic terms, also transitions of vibrational energy into electronic energy. These transitions lead either to dissociation of the molecules from the electron-excited state, or to radiation in the UV of the visible region of the spectrum. It was such a radiation of the OsO_4 molecule which we have observed in the present study by exciting in it oscillations with a CO_2 laser.

2. The following were compared in the experiment: 1) the times of emission produced when the OsO_4 molecules are excited by IR (CO_2 laser) and UV (N_2 laser) emission, and their dependences on the OsO_4 pressure; 2) the spectral distribution of this emission. The vibrational states of the OsO_4 molecule were excited with a frequency-tunable CO_2 laser with a pulse peak of 90 nsec (at half-maximum), with a "tail" of 1.5 μsec . Both single-frequency and two-frequency³ excitations were used. The electronic state of the OsO_4 molecule was excited with a nitrogen laser with pulse duration 15 nsec and energy 100 μJ in the pulse. The pulse repetition frequency could reach 500 Hz, so that luminescence measurements could be made in the photon-counting regime. The OsO_4 was contained in a stainless-steel cell evacuated beforehand to a pressure 5×10^{-5} Torr. The emission lifetimes were measured in succession, first in the ultraviolet then in the infrared, at the same content of the OsO_4 cell.

3. Figure 1 shows the lower electronic terms of the OsO_4 molecule (singlet and triplet) and the scheme of the investigated transitions. The singlet terms were obtained on the basis of an analysis of the electron-vibrational progression of the absorption

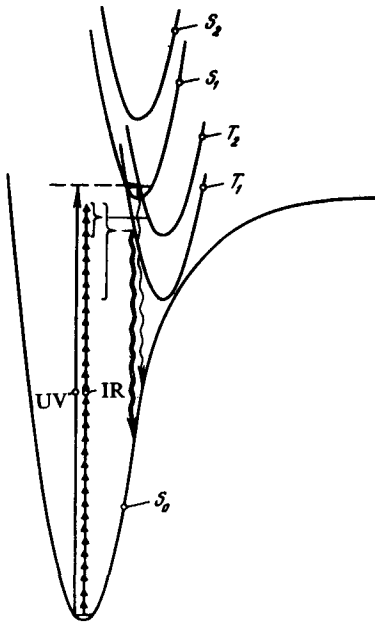


FIG. 1. Scheme of the lower electronic terms of the OsO_4 molecule. The positions of the singlets were obtained from an analysis of the electronic absorption spectra of Ref. 4. The shown approximate position of the triplets is based on the phosphorescence spectrum obtained in the present study following an excitation with an N_2 laser. The arrows indicate the investigated transition schemes.

spectra of Ref. 4. The approximate positions of the triplet states were deduced by an analysis of the phosphorescence spectrum, given below, of OsO_4 excited by a nitrogen laser. An estimate of the lifetime of the very lowest excited singlet state yields $\tau_{\text{lum}} \approx 36$ nsec (see Ref. 4). The position of the dissociation limit shown in Fig. 1 for the ground electronic state relative to the complete-symmetry coordinate is quite arbitrary and was estimated from the known OsO_4 dissociation limit, ~ 30 quanta of the CO_2 laser. The arrows show the schemes of the investigated transitions. It is seen from Fig. 1 that the electronic states of the OsO_4 molecule are strongly intermixed. In Fig. 2

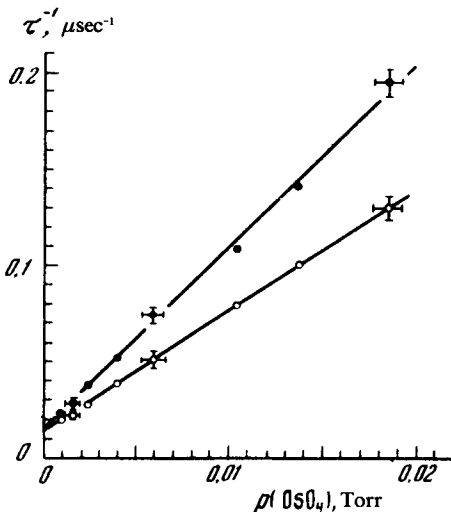


FIG. 2. Dependence of the reciprocal phosphorescence lifetime on the OsO_4 pressure in the cell. The upper straight line was obtained by excitation with an N_2 laser, the lower by excitation with a CO_2 laser (lasing line $P(40)$, 925.0 cm^{-1}). The monomolecular lifetime is $\tau_0(\text{N}_2) = \tau_0(\text{CO}_2) = 75 \pm 15 \mu\text{sec}$. The reciprocal quenching rates are $\tau_q(\text{N}_2) = 102 \pm 10 \text{ nsec-Torr}$ and $\tau_q(\text{CO}_2) = 156 \pm 10 \text{ nsec-Torr}$.

are compared the Stern-Vollmer dependences of the reciprocal lifetime of the emission under IR and UV excitation:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{P}{\tau_q}, \quad (1)$$

where τ is the emission time, τ_0 is the monomolecular lifetime, and τ_q^{-1} is the quenching rate. It is seen from Fig. 2 that monomolecular lifetimes of the phosphorescence are equal, and that the quenching rates are also very close. The small difference in the quenching rates is due to the different methods used to excite the triplet states.

Figure 3 shows the phosphorescence spectra of OsO_4 in response to IR and UV

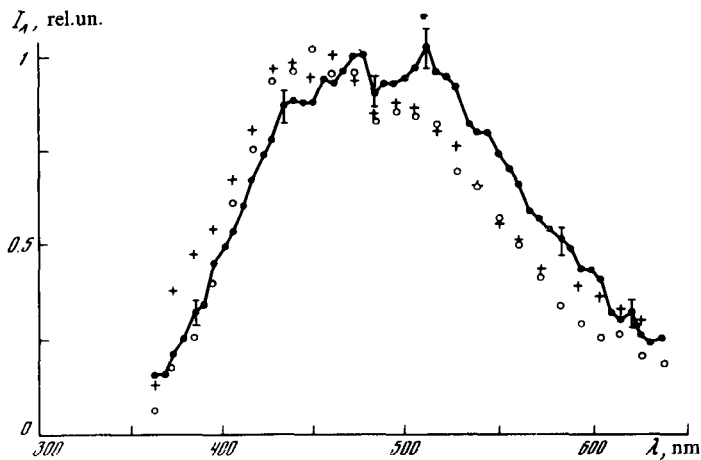


FIG. 3. Phosphorescence spectra obtained by exciting OsO_4 : ●—nitrogen laser, +—two-frequency excitation by a CO_2 laser ($\nu_1 = 947.7 \text{ cm}^{-1}$, $P(16)$; $\nu_2 = 927.0 \text{ cm}^{-1}$, $P(38)$); ○—single-frequency excitation with a CO_2 laser, $\nu_1 = 947.7 \text{ cm}^{-1}$, $P(16)$. The pressure of the OsO_4 in the cell is 3×10^{-2} Torr. The spectral resolution is 40 Å. The correction for the spectral sensitivity of the recording system (MDR-2 and FEU-79 photomultiplier) was not introduced.

excitation, obtained at OsO_4 pressure in the cell 3×10^{-2} Torr. It is seen that these spectra are also in good agreement and have characteristic structure consisting of two maxima at 460 and 510 nm, due apparently to the presence of two closely lying excited electronic states (see Fig. 1). The small difference between the intensities of these maxima is due to the different methods used to excite the triplets.

To prove conclusively that the observed emission is due to the OsO_4 molecule, experiments were performed on the dissociation of OsO_4 by IR and UV radiation at the same emission intensity. Whereas IR did produce such a dissociation (see also Ref. 5), we were unable to observe dissociation under the influence of UV from an N_2 laser even when the number of irradiation pulses was 100 times larger than in the case of IR. This experiment precludes the appearance of emission due to phosphorescence of the radicals produced in monomolecular decay of OsO_4 .

Our experiments thus point unequivocally to the existence of an inverse radiationless transition when OsO_4 molecules are excited in the field of an IR laser. The ob-

served phenomenon is extremely important, first since it makes it possible to study systematically in experiment the non-adiabaticity (of the coupling of the electronic and nuclear motion) under well defined initial conditions of the IR laser excitation. Second, this phenomenon is undoubtedly quite general when molecules are excited by IR lasers, namely, the transitions lead to the appearance of electron-excited fragments when the molecules dissociate. The investigation of this process is therefore of great interest also in the study of IR dissociation itself. Finally, it is of interest to investigate the purely practical aspect of the inverse radiationless transition: production of inversion and lasing in the UV and in the visible region of the spectrum under IR excitation, and also visualization of IR radiation.

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²*Radiationless Processes in Molecules and Condensed Phases*, edited by F.K. Fong, Springer-Verlag, Berlin, Heidelberg, New York, 1976.

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