

VIBRATIONAL RELAXATION OF MOLECULAR GASES IN INTENSE OPTICAL FIELDS

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Received October 4, 1988

The results obtained from optoacoustic measurements on the dependence of the vibration-translation relaxation time in CO₂ and H₂O on CO₂-laser intensity around 10.6 μm are reported. It found that as laser intensity rises, the CO₂ relaxation time decreases, whereas that of water vapour increases.

A knowledge of the dependence of the elastic and inelastic relaxation rates on laser intensity appears to be critical for the study of nonlinear interactions between intense quasimonochromatic radiation and molecular gases.¹⁻³ In particular, this information is required for solving problems pertaining to the nonlinear transfer of optical radiation in molecular gases and the atmosphere, in laser chemistry, and in a number of other areas where the population dynamics involved in the interaction of a medium with laser light plays a decisive role.

A series of experiments (see Ref. 3 and references therein) has shown a considerable increase in the vibration-translation relaxation rate over the case of linear interaction in the resonance excitation of polyatomic (SF₆, CH₃F, CH₃COCOCH₃) molecular gases by intense laser radiation. The measurement data reported by Akhmanov et al.⁴ indicate an increased intermolecular vibration-vibration exchange rate in CH₄:SF₆ and CD₄:CH₄ induced by a CO₂-laser at 10.6 μm. The theoretical analysis of a representative body of the relevant experimental evidence leads one to suggest that the reduced vibrational relaxation time for the strong resonance excitation is due to vibration anharmonicity, intermode and intramode exchanges, and gas heating³. As for the dominant absorbers of optical radiation in the atmosphere, e.g. H₂O, CO₂, NH₃, O₃, no direct measurements are available for the vibrational relaxation rate as a function of excitation intensity.

Our earlier work on CO₂ and H₂O absorptivity in an intense radiation field from a CO₂-laser⁵⁻⁷ has revealed a saturation effect caused by the resonance excitation of CO₂ and the influence of the field on intermolecular interaction processes in the nonresonant case of H₂O. The absorptivity of the gases was found to decrease with increasing laser intensity, although the mechanisms responsible for the observed relations were different. Enhanced transmittance in the far wing of the H₂O spectral line induced by high-intensity radiation from a CO₂ laser may provide indirect experimental evidence for the effect of an intense nonresonance radiation on VT relaxation in water vapor. Physically, it can be explained by the fact that the classical intermolecular interaction potential $V(R)$ is affected by the laser field. $V(R)$ for a high-intensity radiation field has the form⁷

$$V(R) = V_0(R)(1 - b_j I) \quad (1)$$

where $b_j = \frac{1}{\hbar^2 \omega^2 c} \mu \frac{\omega_j^2 |M_j|^2 R^{4/3}}{|\omega - \omega_j|^{2/3} v^{4/3}}$. Here M_j is the j^{th} -line dipole moment matrix element; $R_j = C|\omega - \omega_j|^{1/a}$; ω_j is the j^{th} -line frequency; ω is the laser frequency; c is the velocity of light; v is the mean thermal velocity of molecules; μ , C , a are the parameters involved in the solution to the problem of the line wing absorption in a weak field⁸.

The far wing absorption is determined by the behavior of $F(R)$ and decreases as the laser intensity is increased^{7,8}.

$$\kappa(I) \approx \kappa_0 (1 - b_j I) \quad (2)$$

For $\lambda = 10.6 \mu\text{m}$ and the 010 band of H₂O, b_j is estimated to be $\approx 10^{-7} \text{ W}^{-1}/\text{cm}^2$, which corresponds to $I_{\text{thr}} \sim 5 \text{ MW}/\text{cm}^2$, in a reasonable agreement with experiment. The relaxation rate ω_{VT} also depends on $V(R)$ as does the absorption coefficient. The semiclassical representation method and first-order perturbation theory give ω_{VT} for the molecular-atomic collisions as⁹

$$\omega_{\text{VT}} = \left| \kappa_{\text{VV}}, \int_{-\infty}^{\infty} \frac{V'(R)}{\hbar} \exp\left[\frac{i}{\hbar} (E_V - E_{V'}) t\right] dt \right|^2, \quad (3)$$

where x_{VV} is the matrix element of $x = r - r_e$ (r_e is the mean nonvibrating molecular size); E_V , $E_{V'}$ are the molecular energies in V and V' states, respectively; $V'(R) \sim \alpha V(R)$, where $V(R)$ is the classical intermolecular interaction potential; I/α is the width of the potential well.

It follows from Eq. (3) that the decreased $V(R)$ in a high-intensity radiation field would lead to the decrease in ω_{VT} and, consequently, to an increase in the VT relaxation time. Thus, for the resonance and nonresonance excitation of a molecular gas by intense

optical radiation, the variation of the VT relaxation time is accounted for by different physical mechanisms, which can contribute with opposite signs; that is, the VT relaxation is accelerated during resonance excitation and retarded when the far wing is excited.

Laser excitation results in the absorption saturation at the resonance transition in CO₂, and increased transmittance of the H₂O line wing⁷. The aim of this work is to measure the dependence of the vibration-translation relaxation time in CO₂ and H₂O for resonance and nonresonance interaction with high-intensity pulsed radiation from a CO₂ laser ($\lambda = 10.6 \mu\text{m}$).

THE EXPERIMENT

The dependence of the VT relaxation time in CO₂ and H₂O on the laser intensity at 10.6 μm was measured optoacoustically as shown in Fig. 1. A TEA CO₂ laser (1) with a nonselective resonator generated an output spectrum consisting of 2–3 components, the peak energy (> 80%) being in the P20 line of the 00¹-10⁰ band. The laser emitted single pulses of 300 ns FWHM (~ 1.5 μsec at the base). Increased laser intensity and its uniform distribution over the beam diameter were provided by a lens system (2). The intensity was adjusted by step attenuators (3) and varied from 0.2 to 4.0 MW/cm². The laser output entered a 3 mm ID diaphragm (4), followed by a 10 mm ID optoacoustic cell (5) filled with the gas of interest. The pulse energy passed through the cell was monitored by a calorimeter (6). The pressure pulse due to the optoacoustic effect in the cell was detected by a custom-made flat microphone (7) inserted in the cell wall, preamplified and recorded by an oscilloscope (8).

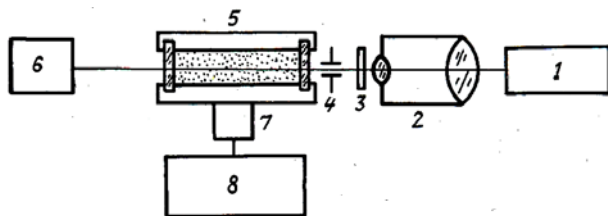


Fig. 1. Block diagram of experimental setup.

EXPERIMENTAL DATA PROCESSING AND DISCUSSION

The information-bearing signal in the optoacoustic pulse excitation measurements is given by the relation:

$$A(P) = \Delta U/E = C\Delta P\varepsilon(P)/E, \quad (4)$$

where ΔU is the electric signal amplitude from a capacitor optoacoustic cell microphone; E is the laser pulse energy; ΔP is the pressure increment due to collisional relaxation; $\varepsilon(P)$ is a coefficient that allows for changes in the elastic properties of the microphone diaphragm as the total pressure p varies; C is a pressure-independent calibration constant.

For low pressures, ΔP is determined by the competition between VT relaxation and deactivation of vibrationally excited molecules at the cell walls. These processes are characterized by the times τ_{VT} and τ_d and rates $w_{VT} = \tau_{VT}^{-1}$ and $w_d = \tau_d^{-1}$, respectively. For a cylindrical cell of length $l \gg r$ (where r is the cell radius),

$$\Delta P = (\gamma - 1) \frac{\kappa l E}{V} F(w_{VT}, w_d, w_T, \tau). \quad (5)$$

Here γ is the adiabatic exponent; κ is the absorption coefficient for the gas of interest; V is the cell volume; F is a function that depends on w_{VT} , w_d and the pulse duration τ , as well as on the thermal relaxation rate w_T for the gas heated by the laser pulse.

For a short-pulse excitation, $\tau \ll \tau_{VT}(P)$, $\tau_d(P)$, $\tau_T(P)$, the F -function has the form¹⁰:

$$F(w_{VT}, w_d, w_T) = \frac{w_{VT}}{w_{VT} + w_d} \left[\frac{w_{VT} + w_d}{w_T} \right] - \frac{w_T}{w_{VT} + w_d - w_T} \quad (6)$$

where $w_{VT} = w_{VT}^0 P$; $w_{d,T} = w_{d,T}^0 / P$ and the superscript "0" stands for the rate constant normalized to a pressure of 1 Torr. The values w_d and w_T are readily calculated, provided the cell radius and the diffusion coefficients for the absorbing molecules in the ground and excited vibrational states are known⁶.

The measurement results are conveniently analyzed by using the optoacoustic detector signal ratio for different pressures, i.e. $A(P_2)/A(P_1)$. The ratio is independent of the absorption coefficient, and hence w_{VT} can be determined from the relation

$$\frac{A(P_2)}{A(P_1)} = \frac{\varepsilon(P_2) P_2 F[w_{VT}(P_2), w_d(P_2), w_T(P_2)]}{\varepsilon(P_1) P_1 F[w_{VT}(P_1), w_d(P_1), w_T(P_1)]} \quad (7)$$

The values of $\varepsilon(P_1)$ and $\varepsilon(P_2)$ are found separately, e.g. by the electric activation technique¹¹. The deactivation and relaxation rates w_d and w_T are calculated for P_1 and P_2 , respectively¹⁰. The pairs of values of P_1 and P_2 used in the measurements were 1 and 3 and 1 and 5 Torr for H₂O and 1.1 and 3 and 1.1 and 5 Torr for CO₂.

The measurements of A for CO₂ were obtained with a maximum intensity of 0.8 MW/cm², which was ≈ 1.5 –2 times as large as the saturation threshold⁵. For the H₂O measurements, the laser intensity was increased to ≈ 4.0 MW/cm², i.e. as high as the threshold level for the enhanced transmittance in the far wing of the 010 band reported by Ageev et al⁶.

The observed and calculated behavior of $A(P_1)/A(P_2)$ for CO₂ and H₂O as a function of the CO₂ laser intensity injected into the optoacoustic cell is shown in Fig. 2. The calculations were made under the assumption that, according to Eqs. (1) and (3), $w_{VT}(I)$ for the 10.6 μm laser excitation of H₂O can be given as $w_{VT}(I) = w_{VT}^0(1 - bI)$, where $b \sim 10^{-7} \text{ W}^{-1}\text{cm}^2$. The

ω_{VT}^0 constant for the 010 vibration in pure water vapor was derived from the measured value of $\tau_{VT} \sim 4 \times 10^{-9}$ s atm obtained by Whitson and McNeal¹². The plots for CO₂ were calculated in a similar way, assuming that the $V-T$ relaxation rate was increased for heavy resonance pumping as is the case with other molecules, e.g. SF₆³. The estimates employed the exponentially decreasing function $\tau_{VT}(I)$ where $\tau_{VT}^0 = 10.8 \mu\text{s atm}^{13}$.

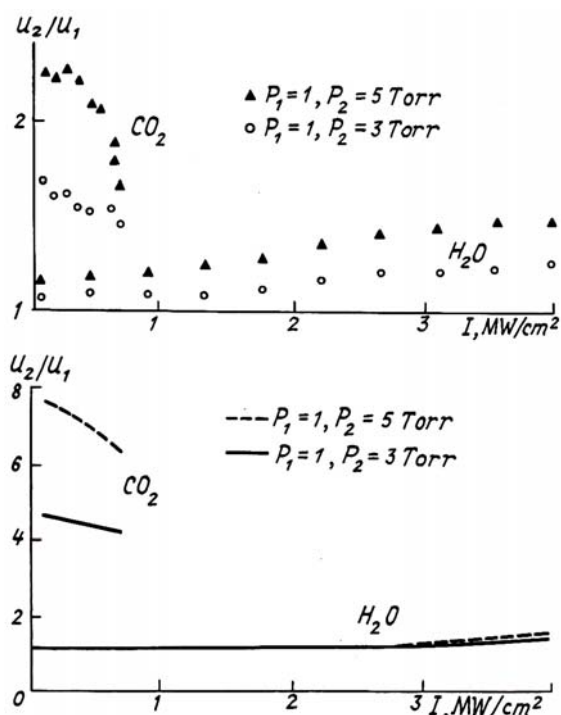


Fig. 2. Optoacoustic signal amplitudes vs. CO₂ laser intensity.

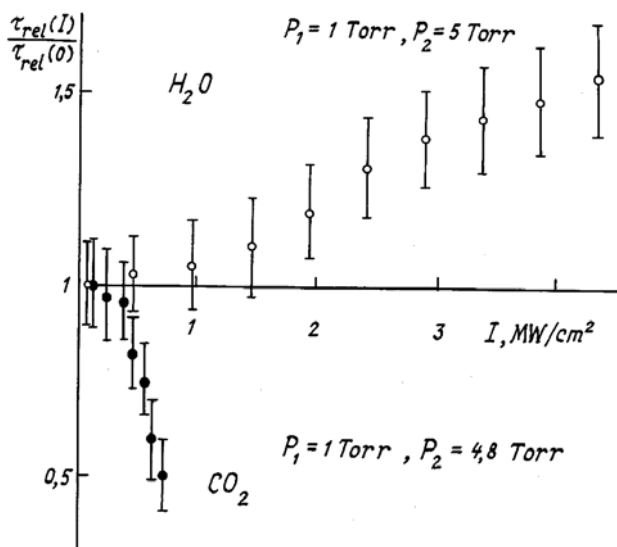


Fig. 3. Vibrational relaxation time vs CO₂-laser intensity.

Both for H₂O and CO₂, the calculations are in qualitative agreement with experimental observations. Quantitative discrepancies may be due to large uncertainties in the assigned values of $\epsilon(P_1)$ and $\epsilon(P_2)$. Using Eq. (7), we derived the explicit behavior of $\tau_{VT}(I)$ for CO₂ and H₂O (see Fig. 3), although the numerical accuracy was not high. The experiment shows a quantitative difference in the nonlinear dependence of the vibrational relaxation in molecular gases for different patterns of interaction between the intense laser radiation and the gas species.

For the resonance excitation, the VT relaxation time is reduced as the laser intensity is increased. For $I \sim I_{\text{sat}}$, $\tau_{VT}(I)/\tau_{VT}(0) \approx 0.6$, which correlates well with earlier observations of the vibrational relaxation behavior in complex molecules^{3,4}. For very large offsets from resonance, characterized by laser absorption in the far wing of the spectral line, the relaxation time is increased; this is especially pronounced when $I \gtrsim I_{\text{thresh}}$ (where I_{thresh} is the threshold intensity for the enhanced transmittance effect to occur). We believe the physical mechanism accounting for this behavior of $\tau_{VT}(I)$ in the nonresonance case to be a decreased molecular interaction potential in the laser field. In other words, it is this mechanism that is responsible for the entire multitude of spectroscopic phenomena involved in optical absorption by spectral line wings, including the specific details of absorption in a the strong field.

ACKNOWLEDGEMENT

The authors are grateful to Prof. S.D. Tvorogov and Dr. B.A. Tikhomirov for stimulating discussions of the experimental program and helpful comments upon the results obtained.

REFERENCES

1. P.A. Apanasevich, S.Ya. Kilin, A.P. Nizovtsev and N.S. Onishchenko *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **49**, 541 (1985)
2. E.N. Chesnokov, V.N. Shcherbinin and V.N. Panfilov *Zh. Eksp. Teor. Fiz.*, **75**, 2066 (1978)
3. S.A. Akhmanov and N.I. Koroteev *Methods of Nonlinear Optics in Light Scattering Spectroscopy* (Nauka, Moscow, 1981)
4. S.A. Akhmanov, V.M. Gordienko and V.V. Lazarev *Izvestiya Akad. Nauk SSSR, Ser. Fiz.*, **42**, 379 (1979)
5. B.G. Ageev, Yu.N. Ponomarev and L.K. Chistyakova *Izv. Vyssh. Uchebn. Zaved., Ser. Fiz.*, No. 10, **49** (1982)
6. B.G. Ageev, Yu.N. Ponomarev and B.A. Tikhomirov *Nonlinear Optoacoustic Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1987)

7. B.G. Ageev, E.P. Gordov, Yu.N. Ponomarev and S.D. Tvorogov *Izvestiya Akad. Nauk SSSR, Ser. Fiz.*, **49**, 459 (1985)
8. L.I. Nesmelova, O.B. Rodimova and S.D. Tvorogov *Spectral Line Contour and Molecular Interaction* (Nauka, Novosibirsk, 1985)
9. V.N. Kondratiev and E.E. Nikitin *Kinetics and Mechanism of Gas-Phase Reactions* (Nauka, Moscow, 1974)
10. O.Yu. Nikiforova and Yu.N. Ponomarev *Izv. Vyssh. Uchebn. Zaved., ser. Fiz.* Submitted to VINITI, No. 4097–1987, **30**, 16 (1987)
11. A.B. Antipov, V.A. Kapitanov, Yu.N. Ponomarev, and V.A. Sapozhnikova *Optoacoustic Method in Laser Molecular Gas Spectroscopy* (Nauka, Novosibirsk, 1984)
12. M.E. Whitson, and R.I. McNeal, *J. Chem. Phys.*, **66**, 2696 (1977)
13. T. Aoki, M. Katayama *Japan. J. Appl. Phys.*, **10**, 1303 (1971)