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Laser-Excited Vibrational Fluorescence of Matrix-Isolated Carbon Monoxide*

H. Dubost, L. Abouaf-Marguin, and F. Legay
Laboratoire de Photophysique Moléculaire, Université Paris-Sud, 91-Orsay, France
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The infrared emission of CO molecules isolated in solid neon and argon matrices has been observed at very low temperature. The optical excitation of carbon monoxide was provided by a Q-switched frequency-doubled CO_2 laser. The fluorescence lifetime τ_F was found to lie in the range 4–8 msec, with no appreciable change of τ_F as the matrix/reactant ratio increased from 100 to 1000. On the other hand, a strong dependence of τ_F with temperature has been observed.

In the past, vibrational relaxation in solids has often been considered to be very fast. Nevertheless, theoretical[1] and experimental studies[2,3] have shown that this is not always the case for small molecules trapped in inert matrices at low temperatures. Particularly, the vibrational relaxation time of N_2 in the $A\,^3\Sigma_u^+$ state has been found to be of the order of 1 sec.[2] None of these studies has involved the infrared-laser excitation technique which has been widely used to excite vibrationally molecules in the gaseous phase.[4]

We report here experiments showing the vibrational fluorescence of a solid. Infrared emission of carbon monoxide trapped in solid neon and argon has been observed in the region of the fundamental vibration at 4.7 μm. Carbon monoxide and rare-gas (air-liquid purity $\geq 99.99\%$) mixtures were deposited onto a CsBr window. The latter made thermal contact, via indium gaskets, with a copper block at the bottom of the helium tank of a cryostat. The lowest window temperature obtained with this apparatus was about 6°K. Infrared absorption spectra of CO in rare gases have been extensively studied, using a matrix-isolation technique, as a function of the relevant parameters: concentration, deposition rate, deposition temperature, and recording temperature.[5] Because of the sample-preparation technique, it is not possible to give accurate estimates of the film thicknesses. Nevertheless, in view of the total amount of gas deposited and from absorbance measurements, the optical thickness is believed to lie in the range 5–100 μm. Monomeric CO has been found to have an absorption band centered at 2140.9 cm^{-1} in neon and 2138.4 cm^{-1} in argon with a measured bandwidth $\Delta\nu = 0.8$ cm^{-1}. These frequencies fall in the same spectral region as twice that of some CO_2 laser lines. Laser excitation of the first CO vibrational level could therefore be tried.

The experimental setup is shown in Fig. 1. Samples were illuminated with a Q-switched frequency-doubled CO_2-N_2-He laser operating on the $R(8)$ line of the 00^01–02^00 band of CO_2 at 1070.43 cm^{-1},[4] which is exactly half the measured absorption frequency of CO in a Ne matrix. The Q-switch operation was obtained by a rotating mirror, and the rotation speed could be adjusted between 40 and 200 Hz, producing 1–2-kW pulses of 150–500 nsec width. Conversion into the second harmonic at 2140.86 cm^{-1} took place in a 9-mm-thick tellurium crystal with an efficiency of about 1%. The 4.7-μm light was focused by a CaF_2 lens ($f = 5$ cm) onto the sample. The fluorescence was observed at 60° from the excitation and collected by a CaF_2 lens ($f = 4$ cm) onto a pho-

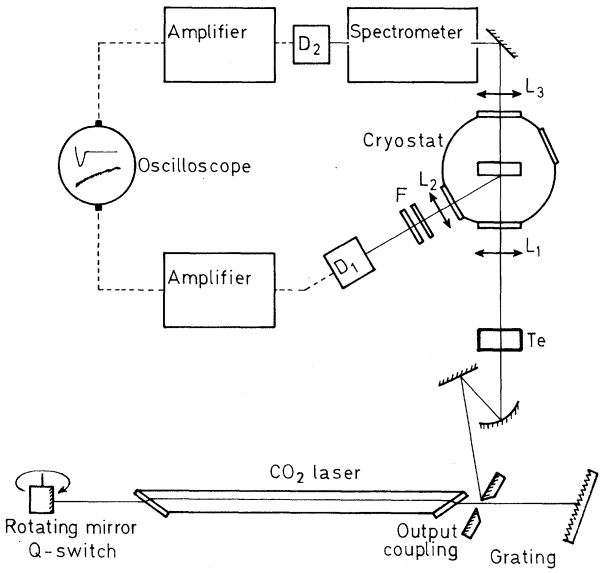

FIG. 1. Schematic diagram of the experimental arrangement. L_1, L_2, L_3 are CaF_2 lenses; D_1, D_2 are Ge-Au detectors (77°K), and F denotes InAs and VIR-3 filters.

toconductive Ge-Au detector with a 150-$k\Omega$ resistive load (response time 20 μsec). The signal was amplified by a PAR model CR4 low-noise amplifier and recorded on a Tektronix model 555 or 564 oscilloscope. The start of the fluorescence signal was always accompanied by a much stronger signal coming from a part of the laser pulse diffused by the matrix and the CsBr window, but this signal was not very troublesome because its duration was very short (20 μsec) compared to the fluorescence decay time.

In all experiments the fluorescence decay was perfectly exponential. Results are given in Table I. In the case of neon matrices, where the mole ratio ranged from 100 to 1000, the fluorescence decay time was found to lie between 6 and 8 msec. The longest decay time was found to be $\tau_F = 8.0 \pm 0.4$ msec with a Ne/CO = 500 sample (Fig. 2). τ_F seemed to decrease when the matrix/reactant ratio and optical thickness were increased. For the CO/Ar case the difference between the excitation frequency and the center of the absorption band was 2.5 cm^{-1}. Nevertheless, for low mole ratio and thick films the wings of the CO band were sufficiently broad to ensure a significant absorption of the laser pulse. The fluorescence was indeed observed from a thick sample of CO in argon with Ar/CO = 100, thus showing that the bandwidth $\Delta\nu$ measured in absorption experiments was due to inhomogeneous broadening. The measured decay time was $\tau_F = 4.1 \pm 0.4$ msec. In the two matrices τ_F was found extremely temperature dependent. For a rise in temperature not exceeding more than 2°K, the fluorescence lifetime was reduced by an order of magnitude. Unfortunately, the temperature measurements performed with a platinum resistance embedded in the copper block were not sufficiently accurate to draw a plot of τ_F versus temperature. Nevertheless, this observation is in agreement with the theoretical prevision of Sun and Rice,[1] which gives a large temperature dependence for the transition rate contrary to the results of Tinti and Robinson[2] in the case of N_2.

TABLE I. Fluorescence decay times τ of CO trapped in solid Ne and Ar at 6°K.

Matrix	Matrix/reactant ratio	Approximative optical thickness (μm)	τ (msec)
Ne	100	5	6.2
Ne	500	15	8.0
Ne	1000	60	6.5
Ar	100	100	4.1

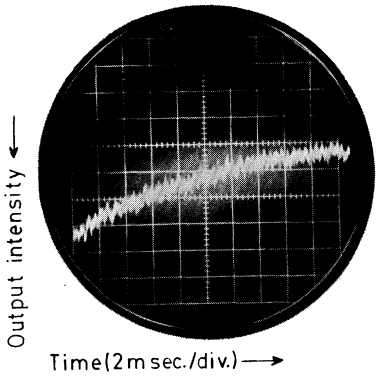

FIG. 2. Typical decay curve for a Ne/CO = 500 sample at 6°K.

The experimental method described in this paper could be a powerful tool for the study of the interaction of molecules with a solid environment. Furthermore, the CO case is an almost ideally suitable two-level system for studies in nonlinear optics. The relaxation time is more than 10^4 times longer than the pulsewidth and the efficient optical path is extremely short, allowing a strong excitation in a small volume. Phenomena like self-induced transparency, photon echoes, and two-photon absorption are expected to be observed in this case and could give additional information on dynamic effects in solids.

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*Work based on the thesis of H. Dubost, to be submitted to the University of Paris-Sud for the Doctorat ès Sciences.

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Frequency Response of Stimulated Thermal Scattering*

A. O. Creaser† and R. M. Herman
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 31 March 1972; revised manuscript received 7 June 1972)

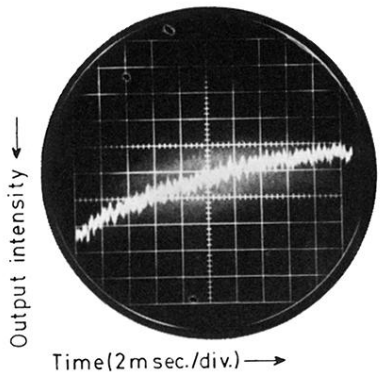
Transient responses for stimulated thermal scattering have been frequency analyzed. Under commonly encountered laboratory conditions, the spectral characteristics for the backscattered light are those predicted through the steady-state theory.

Since its discovery in 1967,[1] several theories of the stimulated thermal scattering of light (STS) have been proposed.[2,3] Inasmuch as the Q-switched laser pulses used to generate the effect are shorter than, or comparable to, the thermal relaxation time associated with this type of scattering, those theories which describe the backscattered optical field in terms of a transient response appear to be quite realistic. The most striking success of the transient theory for backscattering is the prediction of the value for the absorption coefficient necessary for STS to dominate the stimulated Brillouin scattering process (SBS) early in a scattering event.[4]

Despite such success in the time domain, the frequency content of the transient response has actually never been systematically analyzed. In the paper by Bespalov, Kubarev, and Pasmanik (BKP),[2] the peak of the anti-Stokes–shifted scattered-light frequency distribution was estimated to be 0.002 cm^{-1}, while their measured value was small ($\ll 0.02$ cm^{-1}). The steady-state theory, on the other hand, leads to a value equal to the laser-line half-intensity half-width, $\frac{1}{2}\Gamma_L$ ($\simeq 0.1$ cm^{-1} for their experiment). In similar experiments,[5] however, shifts have consistently been found only slightly less than $\frac{1}{2}\Gamma_L$ for similar conditions.

In another important experiment, Darée and Kaiser[6] measured the increase in energy associated with the passage through an absorbing medium of a weak beam in a direction opposite to that of the laser light. The frequency content of the laser and the incident weak beam were identical, except that a small controllable difference could be maintained between their central frequencies. While the amplification as a function of frequency shift was successfully explained using a transient theory, it is also true that the steady-state theory gives similar results for the frequency dependence, in the context in which a band of frequencies associated with the laser gives rise to the amplification of a different band of frequencies[7]—the nonzero bandwidths being associated with the finite pulse duration. Accordingly, while the time-dependent amplification factor must be predicted through transient analysis, the frequency content *per se* may be explainable in a steady-state context.

In the present Letter, we shall frequency analyze the transient response of BKP for square laser pulses, then generalize the analysis to include the cases for which (1) the laser consists of many (axial) modes, giving rise to a linewidth that is large compared with the minimal linewidth $\simeq 2\tau_p^{-1}$, τ_p being the laser pulse duration, and (2) the single-mode laser pulse does not suddenly terminate. It is found that while the BKP frequency shift is correct for an abruptly terminated single-mode laser input, for *all other cases* steady-state results are valid, where the gain contour for monochromatic light is to be convoluted with the laser profile. It should be stressed, however, that the time response is given correctly throughout by the transient theory. We empasize that the restriction to the BKP transient re-



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