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A spectrometer for far i.r. hot broad band fluorescence in gases

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Abstract—An apparatus is described for detecting broad band far i.r. fluorescence in gases pumped by a variety of CO_2 laser lines. It consists of three major components: (i) an Apollo Instruments tunable CO_2 laser, pumping (ii) a specially designed sample cell which collimates the emitted radiation for subsequent analysis in (iii) an N.P.L./Grubb-Parson 'Cube Interferometer', incorporating the Fellgett and Jaquinot advantages. As shown by Roodhardt and Wegdam [1] in HCl pumped via SF_6, the induced far i.r. fluorescence is *rotationally* very 'hot', i.e. the distribution of the rotational absorption envelope peaks at an equivalent temperature of some *thousands* of Kelvin, and is no longer describable by Blotzmann statistics. We present experimental evidence for broad band, far i.r., CO_2-induced fluorescence in the asymmetric top CH_2CF_2 for different CO_2 laser lines. The results are discussed in terms of a model of the collisional dynamics involved in the transfer of vibrational to rotational energy.

INTRODUCTION

Roodhardt and Wegdam [1] have recently described how the far i.r. laser-induced rotational fluorescence in HCl differs greatly from the corresponding absorption envelope at ambient temperature. This is effectively a new method for studying in detail the mechanism of vibrational dephasing via molecular collisions which transfer the energy of the excited molecule from vibrational to rotational, or more accurately, rotovibrational. By using the Master equation appropriate to the system it is possible in principle to find out a great deal about the dynamics of bimolecular interactions.

Motivated by this work, we have decided to construct a spectrometer with which it is possible to study the far i.r. *broad-band* fluorescence of molecular gases induced by several (up to 85) CO_2 i.r. laser lines. We are not in the business of constructing far i.r. lasers which of course produce monochromatic radiation at submillimetre frequencies using such devices as resonance cavities. Our system is easily adaptable, however, for this purpose.

The purpose of this short communication is to describe the apparatus, indicate typical results for the asymmetric top $CH_2{=}CF_2$, and develop the necessary theory to the point where detailed molecular dynamics may be incorporated.

EXPERIMENTAL

The spectrometer is sketched in outline in Fig. 1.

(*i*) Module A is an Apollo Instruments model 560 CO_2 laser, Brewster window-plane grating, tunable over some 85 lines at up to 50 W CW output at a single CO_2 transition. In principle, for each of the 85 lines, the far i.r. broad band fluorescence will be different in character as the CO_2 laser output is tuned from 9.17 to 10.91 μm. At least 40 W output power, TEM_{00} mode, is available at more than 25 wavelengths with 50 W typical at the stronger transitions. The laser is used CW, chopped to provide a reference signal for the Brookdeal lock-in amplifier of our detection system. The chopping rate is variable up to 1 kHz. A fine tuning mechanism allows frequency adjustment by piezoelectric translation of the gratings. For time resolved measurements we may use the laser in *Q*-switch mode, with pyroelectric detection apparatus.

(ii) Module B is a far i.r. cavity which is used when the instrument is working in submillimetre-laser mode. We do not discuss this aspect in this paper.

(*iii*) The sample cell *F* has been designed by one of us (G. J. Evans) to collect collimated far i.r. fluorescence reflected from the parabaloid gold plated wall *G*. This mode of operation is aided by focussing with a germanium lens *C*. *D* is the germanium exit window of the sample chamber allowing the CO_2 radiation to fall onto a power meter *E*. The fluorescence is filtered by the exit window *K*, which separates the sample cell from a Grubb-Parsons/N.P.L. 'Cube' interferometer [3]. This consists basically of

(iv) A melinex (poly ethylene terephthalate) beam splitter *H* which works only in the range 20–240 cm^{-1}, and therefore doubles as a filter.

(v) Fixed and movable front aluminised plane mirrors *I* and *J*, used to produce an interferogram of collimated fluorescence.

(vi) An exit plano-convex polythene lens/filter *L* which focusses onto a Golay detector and associated detection gear *M* (lock-in amplifier, analogue to digital converter, encoder, computer (or microprocessor)). For phase modulation, a reference can be taken by jittering *J* on a loud-speaker spindle. Otherwise the reference is taken from the laser electronics cabinet *P*.

By using polythene filters and a melinex beam-splitter we make sure that only far i.r. radiation reaches the Golay window, which is itself a filter (crystalline quartz). The 'instrument function' may be estimated by substituting a black-body source for *F*—usually a high-pressure mercury Hpl6 arc encapsulated in quartz. The final fluorescence spectrum is therefore a ratio of sample (*F*) and background (black body) interferogram. In principle, for each molecular specimen, the far i.r. induced-fluorescence can be measured for each of the 85 laser lines at different sample pressures (usually of the order of 10^2 Torr).

RESULTS

At the development stage, it is interesting to record the luminous flux intensity of the fluorescence as a function of the intensity at *E* for some

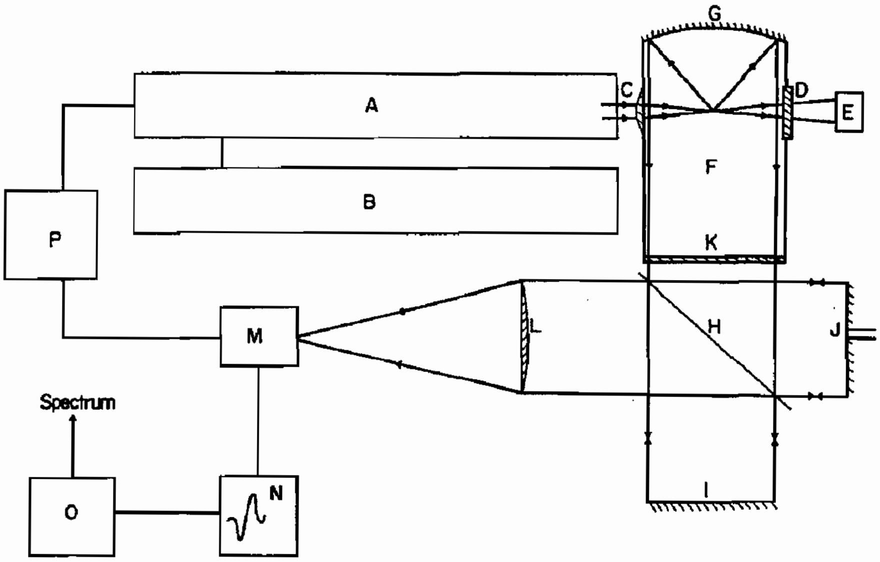

Fig. 1. Schematic diagram of the far i.r. fluorescence spectrometer. (A) Tunable Apollo instruments CO_2 laser, used in chopped C.W. mode on up to 50 different lines. (B) Far i.r. cavity module of the laser. (C) Germanium lens to focus the output laser beam. (D) Germanium exit-window for the CO_2 beam. (E) Power meter for exit beam. (F) Sample cavity, evacuable to mTorr. Typical working pressure of 100 Torr. (G) Parabaloid wall of sample chamber, gold plated. Collimator of far i.r. fluorescence. (H) Melinex beam splitter of 'Cube' interferometer. Range 20–240 cm^{-1}. (I) Fixed front aluminised mirror of the 'Cube'. (J) Moving mirror (stepped) of 'Cube'. (K) Polythene filter/exit window of the sample chamber. Filters out fluorescence above approx. 300 cm^{-1}. (L) Plano-convex filter/exit lens of the 'Cube' interferometer. (M) Electronics of interferometer. (N) Recording apparatus for plane or amplitude modulated fluorescence interferograms. (O) Main-frame computer or micro-computer (Research Machines 380 Z) for Fourier transformation of interferogram. (P) Electronics of the CO_2 laser, used to provide the reference signal for a Brookdeal lock-in amplifier.

CO_2 lines. This is done in Table 1 below for CH_2F_2 at various pressures. Typical phase modulated interferograms of the fluorescence reaching the Golay detector are illustrated in Fig. 2. The interferogram is distinctly different from that of the CH_2CF_2 far i.r. absorption spectrum at room temperature. These interferograms were obtained with the 10.24 μm line of the laser, and in principle 84 others are attainable with the same instrument.

In Figs 3 and 4 we illustrate respectively the absorption intensity $\log_e I_0/I$ (see Table 1) vs wavelength of the CO_2 pumping line for CH_2CF_2 and the total detected fluorescence signal (in mV) for each line. The two distributions are different and there is no indication of stray light effects, having been eliminated by the design of the sample cell.

DISCUSSION

As indicated by ROODHARDT and WEGDAM the far i.r. fluorescence of HCl (excited via SF_6) from the rotational states in the vibrational ground-state cannot be explained by a Boltzmann distribution of the $J+1 \rightarrow J$ transitions even at very high temperatures. From the spectra, it is possible to calculate relative changes in the rotational state populations under irradiation. These remain unaltered with the density changes. This suggests a time evolution for the rotators where the peak at high J collapses into a room-temperature Boltzmann distribution via a double peaked distribution. In order to corroborate this picture the rates of energy transfer to and from the rotators were calculated by a master equation [1]:

$$\frac{dn_J}{dt} = \sum_{J'} (K_{J'J} n_{J'} - K_{JJ'} n_J) \qquad (1)$$

where $K_{J'J}$ is the rate of energy transfer from the rotators making a transition from J' to J. The rate constants satisfy the detailed balance condition:

$$K_{J'J} = [(2J+1)(2J'+1)] \exp(-\Delta E/kT) K_{JJ'}$$
$$\Delta E = E_J - E_{J'}.$$

In treating HCl only $\Delta J = 1$ transitions are taken into account, but for CH_2CF_2 the situation is more complicated. In a future paper we provide a theory for this near symmetric top, and provide a simulation for the expected $\Delta J = 1$ profile shift for CH_2CF_2 on the model of ROODHARDT and WEGDAM.

The theoretical problem posed by the far i.r. rotational fluorescence band involves the description [4, 5] of the unstable state of the molecule excited by the CO_2 radiation pumping one of its vibration-rotation levels in the i.r. This can be designated as the excited state $|e\rangle$. This interacts within the molecular framework with the dense set of states $\{|m\rangle\}$ which includes the pure rotational

Table 1. Throughput and fluorescence cross-sectional intensity for some of the 85 lines accessible

Wavelength of CO_2 line (μm)	I_o/watts (no cell)	I/watts (cell & sample)	Total* far infra-red fluorescence /mV
10.86	0.1	1.2	0
10.835	0.22	3.5	2.56
10.815	0.08	3.3	1.69
10.812	0.24	4.2	3.64
10.81	0.24	4.6	4.50
10.795	0.14	2.2	0
10.793	0.25	3.2	1.57
10.785	0.50	4.3	2.64
10.78	0.65	3.0	3.50
10.718	0.70	8.0	6.72
10.645	0.58	9.0	7.39
10.565	0.80	9.0	3.45
10.528	1.00	9.2	4.80
10.51	1.1	9.6	3.39
10.508	1.2	9.4	4.86
10.496	0.5	6.0	1.45
10.487	1.3	9.0	3.64
10.47	1.4	8.0	1.90
10.455	1.2	6.4	2.12
10.44	0.5	5.0	0
10.375	0.25	2.0	0
10.37	0.50	2.9	0.28
10.362	1.0	4.4	0.70
10.347	1.7	7.8	1.30
10.345	1.5	6.1	1.09
10.342	1.0	5.6	0.12
10.335	2.0	8.2	1.76
10.317	2.35	8.8	1.68
10.316	2.30	8.8	1.70
10.29	1.40	1.8	1.35
10.245	2.50	8.0	1.58
10.218	2.70	7.8	2.26
10.203	2.80	6.8	1.64
10.175	2.8	7.4	1.32
10.135	1.5	1.8	0
10.13	1.4	2.5	0
9.755	0.15	0.2	1.46
9.736	1.2	1.7	2.98
9.718	2.0	2.6	4.87
9.697	2.0	4.0	3.75
9.69	2.5	4.2	6.46
9.676	2.75	7.4	5.12
9.655	3.2	6.5	6.88
9.618	3.4	9.8	5.78
9.612	1.8	6.4	4.57
9.594	2.0	8.0	6.49
9.55	3.5	8.4	5.72
9.535	3.4	9.8	4.77
9.518	3.2	10.1	2.43
9.501	3.1	11.4	2.44
9.355	2.0	6.4	0
9.353	2.6	4.4	0.11
9.316	3.0	10.4	1.16
9.305	3.0	10.0	0.71
9.294	3.0	10.8	0.92
9.285	3.2	10.4	1.02
9.236	2.7	6.4	0
9.228	2.8	6.0	0

* Grand max of phase modulated interferogram.

states in the far i.r. The bath of all other molecules can be described as a dissipative continuum $\{|\epsilon\rangle\}$, introduced to account for molecular collisions and intermolecular potentials, which can be treated as hard spheres in a first approximation. The manifold $\{|\epsilon\rangle\}$ can affect both $\{|m\rangle\}$ and $|e\rangle$ by molecular collisions. The problem is therefore twofold:

(i) To use a theory of line broadening (preferably non-Markovian) to broaden the set of far i.r. fluorescence lines by introducing either statistical

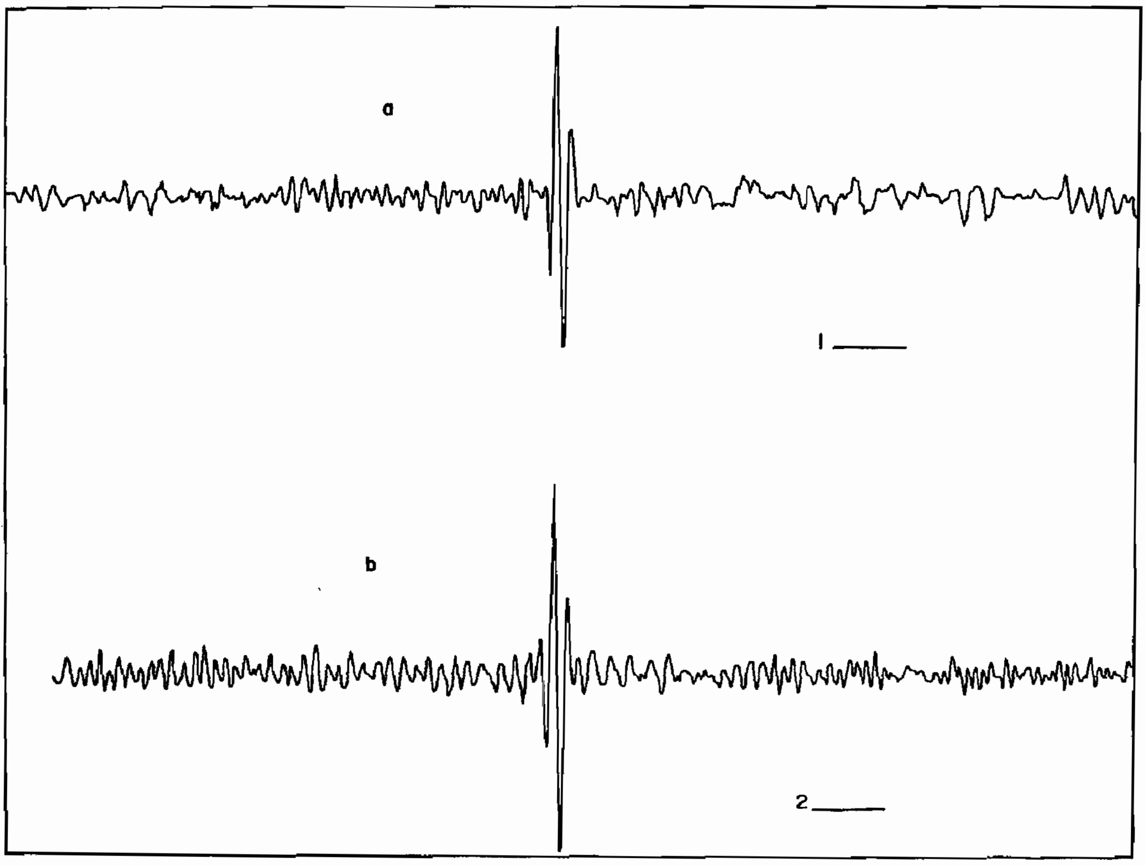

Fig. 2. Phase modulated interferograms of the far i.r. broad-band fluorescence of $CH_2{=}CF_2$. (a) 40 Torr; (b) 240 Torr. (1) and (2) indicate the noise levels. The interferograms are both detailed far out into the winds which means in turn that the spectrum is detailed with $J+1 \rightarrow J$ emission lines at both 40 and 240 Torr. The shapes of the two interferograms are different around the grand-maximum which indicates a shift in the maximum of the rotational emission lines in the far i.r.

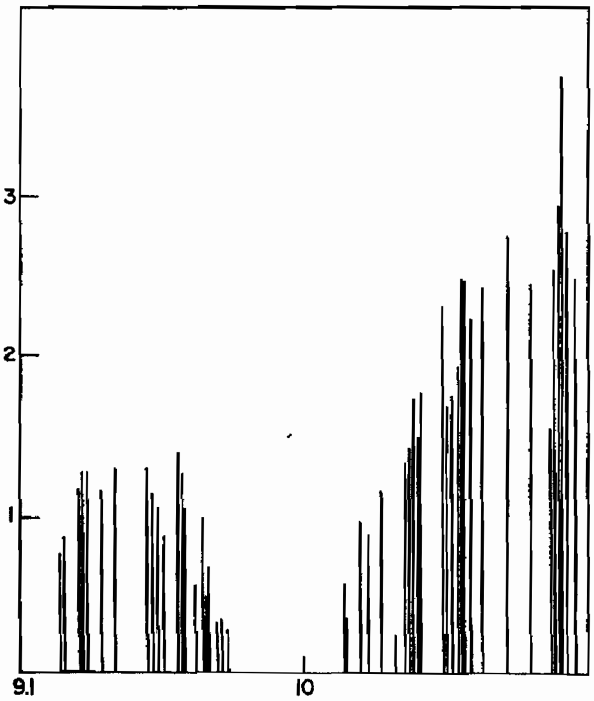

Fig. 3. Distribution of $\log_e(I_0/I)$ (of Table 1) vs wavelength of CO_2 pumping line in μm.

mechanical Mori theory or one of multiplicative stochastic processes. In this way a whole range of molecular collisional modelling can be brought to bear on the interpretation of the fluorescence profile.

(ii) To develop a non-Markovian theory of the decay of fluorescence in the far i.r. induced by a mid i.r. CO_2 laser frequency.

The problem can be put succinctly by stating that in the absence of $\{|\epsilon\rangle\}$ we would have a discrete set of far i.r. fluorescence lines, unbroadened by the interaction of molecular potential energy surfaces. The presence of $\{|\epsilon\rangle\}$ leads to a broadened fluorescence contour, the description of which requires a complicated statistical mechanical theory of the interaction of molecules in a vibrationally excited state, as described by the massive shift of the rotation peak frequency. If we define a state variable A (quantum mechanical or semi-classical) associated with the far i.r. fluorescence this obeys the projected Liouville equation:

$$\frac{d}{dt}A(t) = -i\Omega A(t) + \int_0^t \Phi(t,s)A(s)\,ds + f(t) \quad (2)$$

where Ω is a resonance operator, defined by Mori

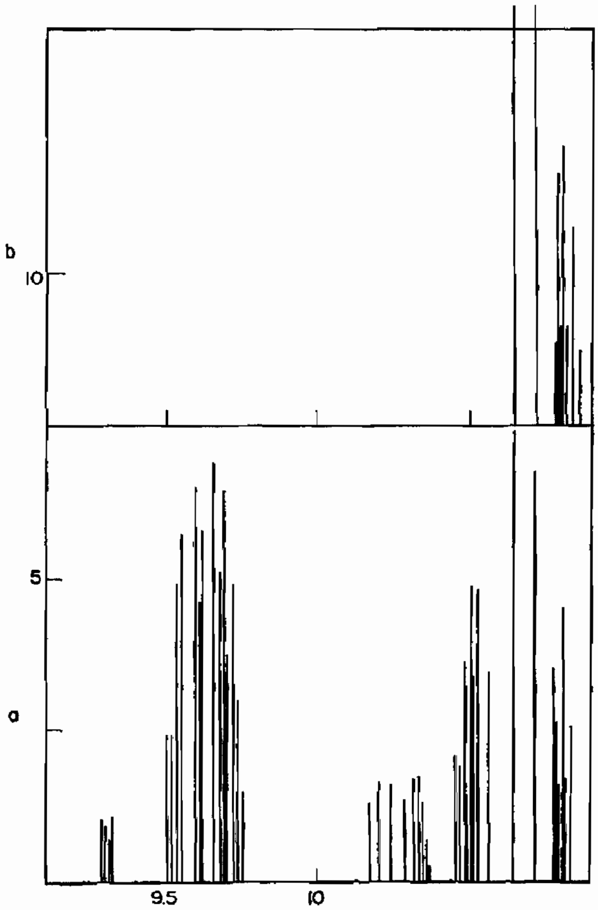

Fig. 4. Fluorescence signal (measured by the interferogram grand maximum signal in mV) vs wavelength of pumping line in μm. (a) 40 Torr CH_2CF_2; (b) 100 Torr CH_2CF_2.

and others, $\Phi(t, s)$ a memory kernel and $f(t)$ a projected force. We have developed methods [5] for handling this type of equation in the presence of arbitrarily high laser fields, where linear response theory is inapplicable. A class of line-broadening models such as 'extended diffusion' has been described by Evans *et al.* [2] inside the structure of Equation 2. These include the J diffusion model, and in a slightly different context the m diffusion model of Gordon. The problem at hand is however of considerably greater potential interest because of the possibility of obtaining different fluorescence spectra (or correlation functions $\langle A(t)A^*(0)\rangle$), from many of the 85 available laser lines (Table 1) per fluorescing sample.

In future work the experimental and theoretical methods described above will be applied to molecules such as $CH_2{=}CF_2$, MeOH and HCl/SF_6, which fluoresce strongly in the far i.r.

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