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Observation of dynamically induced fluctuations of the photon flux and resolution of the broad luminescence band of Cs_2TeBr_6

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A frequency-selective photon correlation experiment is carried out using the 10 K emission of microcrystalline Cs_2TeBr_6 as an example. The recording of dynamically induced *D*-fluctuations allows to resolve the vibrational fine structure of an electronic transition which is not obtained by usual emission spectroscopy at this temperature. The experimental findings support the physical relevance of Prigogine's star-unitary transformations.

Key words: *D*-fluctuations—Prigogine's microscopic theory-photon correlations—resolution of emission spectra

1. Introduction

Dynamically induced fluctuations (*D*-fluctuations) in stationary luminescence processes have been predicted recently [1] from a procedure based on Prigogine's microscopic theory of irreversibility [2]. In particular, it has been shown [3, 4] that *D*-fluctuations of molecular emission are due to dynamic coupling to the environment and that detection carried out by a photon counting experiment leads to resolution of the vibrational structure of broad luminescence bands. The

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Dedicated to Professor Dr. Hermann Hartmann on the occasion of his seventieth birthday use of the new spectroscopic method has been demonstrated for organic compounds in solution at room temperature [3] and by a 10 K luminescence measurement for an inorganic compound in the solid state [4]. The degree of fluctuation (fluctuation measure) $p[f]$ was obtained relating the number of photons registered during a certain time gate Δt_g with the corresponding Poisson probabilities. The variation of $p[f]$ with the energy of the emitted photons corresponds to a spectrum exhibiting vibrational structure. For Cs_2TeBr_6 the photoemission arises from an electric dipole allowed $\Gamma_4(^3T_{1u}) \rightarrow \Gamma_1(^1A_{1g})$ transition which is coupled to the e_g mode of the octahedral complex $[TeBr_6]^{2-}$ due to a Jahn-Teller effect in the excited state ($T \times e$ coupling). At temperatures higher than 10 K the usual emission intensity spectrum is unresolved with no indication of structure, whereas at 2 K temperature the expected vibrational fine structure showing a progression in units of about 150 cm^{-1} quanta is detected. The same structure, however still with a much lower degree of accuracy, has been found in the $p[f]$ spectrum of this compound [4].

In the present note another experimental method will be reported which allows a more accurate measurement of D-fluctuations. It observes the frequency of emitted photon pairs which are correlated by the time intervals between successively registered photons and selects all pairs which are separated by a certain time equal or less Δt. These photon pairs depend on their photon energy and display the vibrational structure, whereas the spectrum of the total number of registered photon pairs combining all time intervals Δt together is unresolved.

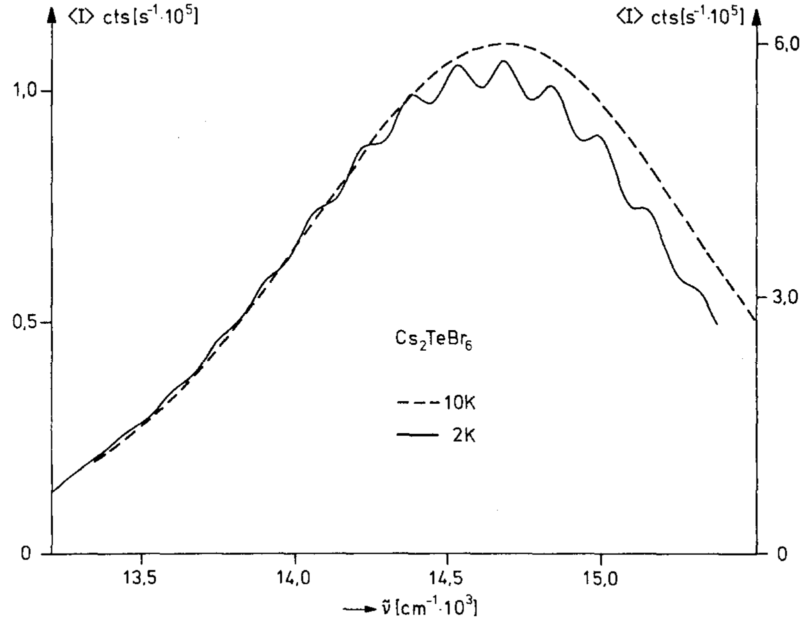

Fig. 1. 10 K and 2 K luminescence spectra of microcrystalline Cs_2TeBr_6 obtained from usual photon counting experiment. The spectral resolution is lower than 4 cm^{-1}

2. Experimental

The experimental device was similar to that reported earlier [4]. The excitation of the microcrystalline Cs_2TeBr_6 was achieved by the 454 nm line of a Spectra Physics 165 Ar^+ laser and a different type of photomultiplier (RCA 7102) has been used in order to detect larger mean values $\langle I \rangle$ (photon registrations per second). Spectral resolution was always lower than 4 cm^{-1}.

The amplified photon pulses were discriminated and fed to START and STOP inputs of an Ortec 457 TAC (time to amplitude converter). For technical reasons the START was always delayed 80 ns compared to the STOP signal. The analog output of the TAC, which is proportional to the time difference between registration of two successive photons, was stored by a Nuclear Data ND 66 MCA in the PHA (pulse height analyzing) mode using an 80 MHz ADC ND 575. For each photon energy the distribution of time intervals Δt of photon pairs was accumulated within a certain preset time t (typical 30 seconds) and stored in the computer memory. Increments between two time intervals which could be distinguished were less or equal 0.2 ns. Mean values $\langle I \rangle$ have been recorded separately. Due to losses during the minimum delay of 80 ns and dead times of about 7.5 μs in the TAC after a "true event", i.e. a TAC output signal, the total number N_p of registrated photon pairs was about one third of $\langle I \rangle \cdot t$.

3. Results

The D-fluctuations are detected through measurement of the relative frequencies $f(\Delta t)$ for the occurrence of the time interval Δt between successively registrated photons. From these the cumulative relative frequencies are calculated for some representative values of Δt:

$$c(\Delta t) = \int_0^{\Delta t} f(t)\, dt. \tag{1}$$

The quantity $c(\Delta t)$ represents the relative frequency for the event that two successively counted photons are registered within a time distance equal or less Δt.

Fig. 2 shows the spectral dependence of $c(\Delta t) \cdot N_p$ for some values of Δt, where N_p is the total number of accumulated events ($N_p \cong \langle I \rangle \cdot t/3$, cf. Sect. 2). The energy dependence of N_p is given by the solid line in the Figure indicated by $\Delta t = \infty$ where the cumulative relative frequency becomes $c(\infty) = 1$. The scale on the left holds only for the lowest $c(\Delta t) \cdot N_p$-spectrum, the other spectra are shifted to lower scale by different reduction factors.

Standard deviations were obtained by averaging over 32 measurements for each photon energy; corresponding error bars are comparable to the size of the symbols used in the Figure.

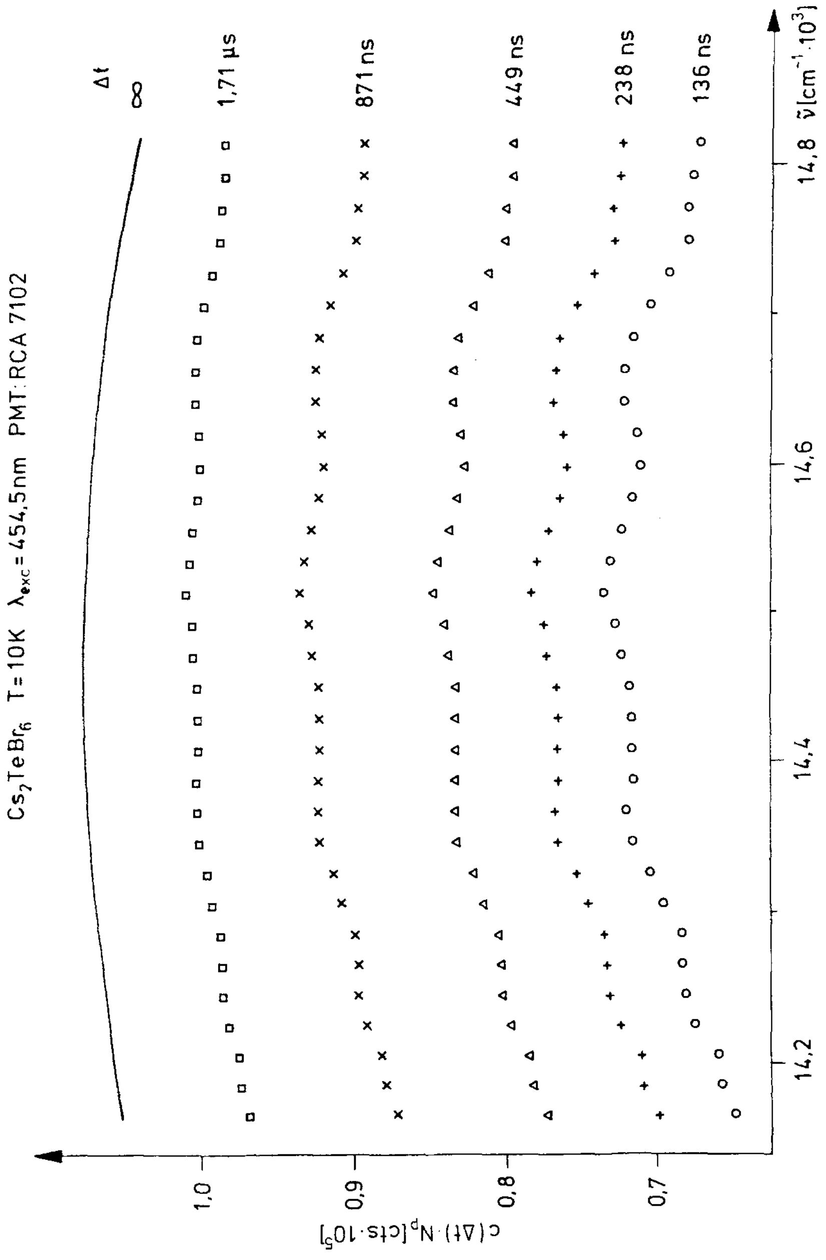

Fig. 2. $c(\Delta t) \cdot N_p$ spectra of Cs_2TeBr_6 at 10 K for different Δt. The spectrum indicated with $\Delta t = \infty$ corresponds to the total number N_p of registrated photon pairs

4. Discussion

For a stationary photoemission process the probability $p(\Delta t)$ for the occurrence of the time interval Δt between successively counted photons can be approximated by the intensity autocorrelation function [5], i.e.

$$p(\Delta t) \simeq \langle I(0) \cdot I(\Delta t)\rangle / \langle I\rangle^2 \tag{2}$$

where $I(t)$ is the intensity at the time t; $\langle I\rangle$ is the mean intensity, i.e. the mean number of counted photons per second. At stationary conditions the relation $\langle I\rangle = \langle I(0)\rangle = \langle I(\Delta t)\rangle$ holds. Eq. (2) is well fulfilled if the average counting rate is sufficiently low, i.e.:

$$\langle I\rangle \cdot \Delta t \ll 1. \tag{3}$$

The data presented in Fig. 2 are obtained from $\langle I\rangle = 1.5 \cdot 10^5$ counts per second. For the Δt values used for the present investigation $\langle I\rangle \cdot \Delta t$ is calculated between 0.05 and 0.68 for $\Delta t = 136$ ns and 1.71 μs, respectively. Therefore, the validity of Eq. (2) can be adopted at least for small values of Δt which are of particular relevance to our main object, the resolution of the vibrational structure. For a large number of measurements ($N_p \simeq 4 \cdot 10^6$, cf. Sect. 2) the relative frequencies $f(\Delta t)$ approximate the probabilities $p(\Delta t)$ sufficiently well. Thus, the cumulative relative frequencies $c(\Delta t)$ approximate the probability that the time between two successively counted photons is equal or less Δt. The quality of this approximation is given by the measure how well Eq. (2) is fulfilled.

The measured relative maxima (or minima) in the $c(\Delta t)$-spectra (N_p is almost constant at least between two neighboring relative extrema in Fig. 2) may be considered arising from a specific "bunching" (or "antibunching") effect between the photons of the corresponding energy. Obviously, the relative maxima in the $c(\Delta t)$ spectra are more pronounced for smaller values of Δt, indicating vanishing photon correlations for larger Δt, with the limit at $\Delta t = \infty$ yielding a spectrum which corresponds to the usual emission.

Photon correlations as manifested by $c(\Delta t)$ measurements also cause variations from Poisson photon distributions which are used for fluctuation measures $p[f]$ if the time gate Δt_g is of the order of (or less than) the photon correlation time [6]. Therefore, measuring $c(\Delta t)$ and fluctuations $p[f]$ should lead to the same results regarding properties which are determined from informations carried along by photon correlation. All data obtained from correlation measurements, the fluctuation measure at 10 K, and from the 2 K usual emission spectrum accordingly yield a vibrational quantum of about 150 cm^{-1} for the progression which is expected for the e_g mode of the complex octahedron. The relative extrema of the 2 K usual emission and the $c(\Delta t)$ spectrum are found at identical wave-numbers (compare Figs. 1 and 2), whereas the $p[f]$ spectrum from Ref. [4] is shifted by a small amount to higher energy. This difference may be explained by experimental uncertainties in recording $p[f]$ and by unappropriately large time gates Δt_g imposed by the limited electronic devices used in the photon counting experiment.

From these results it can be concluded, that the statistical properties of the emitted photons are manifested by fluctuations in the photon flux which are measured by detecting the bunching effects of photons at given photon energies. These dynamically induced fluctuations must be regarded to be caused by the (non-adiabatic) couplings between the "pure" vibrational states of the emitting system due to interactions with the environmental medium. Determining the statistical behavior of the photons of stationary emission processes is of great importance to the theory, as well, since it is able e.g. to justify Prigogine's concept of star-unitary transformations. Its practical use seems to be beyond any doubts.

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