

Vibrational structure of complex compound emission spectra measured by dynamical photon flux fluctuations as predicted in quantum theory of irreversible processes

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The 10 K emission spectrum of Cs_2TeBr_6 was measured by recording the fluctuating photon flux. Since this fluctuation, according to the theory, is due to the dynamic coupling of the molecular system to the environment controlling the dissipation of energy, it should depend on the frequency of the emitted photons. By this, the vibrational structure of the transition has been resolved which could not be obtained by usual emission spectroscopy.

Key words: Complex compounds—luminescence—vibrational structure—dynamical fluctuations

1. Introduction

Recently the removal of Prigogine degeneracy, arising from the dual role of the Hamiltonian which provides the energy levels and the time evolution as well, has been proposed using a star-unitary dynamical transformation D which does not introduce an additional time dependence but contains a new operator τ of the “intrinsic time” for a “well-defined” subsystem evolving with time [1]. The irreversible component of the time evolution of the density operator $\partial D\rho(t)D^{-1}/\partial\tau$ should cause, as predicted, certain specific dynamical fluctuations of photon flux in radiative emission [2]. The observation of these D -fluctuations has been already reported in the case of fluoranthene emission dissolved in various media [3].

In this article we want to report a similar experiment which also uses the new frequency-selective photon counting method by applying it to an emission measurement of an inorganic compound in the solid state at low temperature. Since the dynamical fluctuations carrying along information about the vibrational properties of the molecule depend on the frequency of the emitted photons, it should be possible to detect vibronic structure in the broad band luminescence which by usual emission spectroscopy cannot be resolved. Assigning vibrational fine structure to an electronic transition is the basis for determining molecular geometries in the excited state [4, 5]. Therefore, it would be important to identify at least the vibrational quantum underlying the vibrational progression in emission.

Solid state emission spectra of inorganic compounds usually show even at low temperature broad and unresolved bands, if the transition arises from a change in electronic configuration. Only for relatively few cases the vibrational structure can be resolved. One of the examples where this has been obtained for a system displaying an s - p transition is Cs_2MX_6 ($M = \text{Se, Te}$ and $X = \text{Cl, Br}$) [6]. The emission arises from a dipole-allowed $\Gamma_4(^3T_{1u}) \rightarrow \Gamma_1(^1A_{1g})$ transition which due to a Jahn-Teller effect in the excited state is coupled to the e_g mode of the complex octahedron. The resulting vibrational progression is well resolved for the Se microcrystalline compounds, for Cs_2TeCl_6 only single crystal spectra at 10 K show a fair amount of vibrational structure, and Cs_2TeBr_6 exhibits a broad band emission spectrum with no indication of structure. Since a vibrational progression is well resolved at temperatures near 2 K (cf. Fig. 1), this compound is a good example for applying the new experimental technique.

2. Experimental

The experiment has been carried out using a Mercury high pressure lamp as excitation source and a liquid Helium flow or bath cryostat for cooling the sample to a temperature of about 10 K and 2 K, respectively. The emitted radiation was analyzed by a GCA McPherson 0.5 m double monochromator, a thermoelectrically cooled RCA C31034 photomultiplier and a photon counting system composed of a preamplifier and amplifier/discriminator PRA 1763/1762. A Nuclear Data ND 66 MCA operating in the multichannel scaling mode stored the registered photons (events) during a chosen time gate Δt_g . For a given number of s channels (scans) the distribution of the relative frequencies f_i of i events during Δt_g is calculated by $f_i = n_i/s$ where n_i is the number of channels which contain i events. The mean value N of events during s scans which provides the regular intensity is also calculated. For measuring the fluctuations we use the expression [2, 3]

$$p[f] = \exp\left(-\sum_i f_i \ln(f_i/p_i)\right)$$

with the Poisson probability p_i for the registration of i events with the mean value N . Each measurement with s scans is performed at various energies of the

emitted photons. In addition each single measurement at a given photon energy is repeated several times in order to obtain mean values of $p[f]$ and standard deviations.

3. Results and discussion

In Fig. 1 the resulting $p[f]$ spectrum for a time gate Δt_g of 10^{-5} sec is shown. Each point is averaged over 32 single measurements and each measurement consists of $s = 3072$ scans. Our present equipment limits the maximum effective scan rate to about 75 per second. Long time instabilities of the lamp intensity, of the electronic detection system, and short time intensity variations as well, introduce large error sources that it was decided to restrict our measurements on a rather small spectral region as indicated on the Figure. Relative standard deviations are less or equal to 0.018% which should be small enough for detecting a distinct structure in the $p[f]$ spectrum. The error bars do not decrease significantly when the two measurements with the largest deviations from the mean value are disregarded. The curve which is drawn in the Figure is a line shape function similar to that used for usual vibronic spectra [6] which was fitted to the experimental data by a least squares method using the halfwidths of the contributing line shapes and the quantum of the progressional mode as parameters. The period in the frequency was calculated to be about 145 cm^{-1} which agrees well with the 151 cm^{-1} Raman result [7] obtained from a powder spectrum

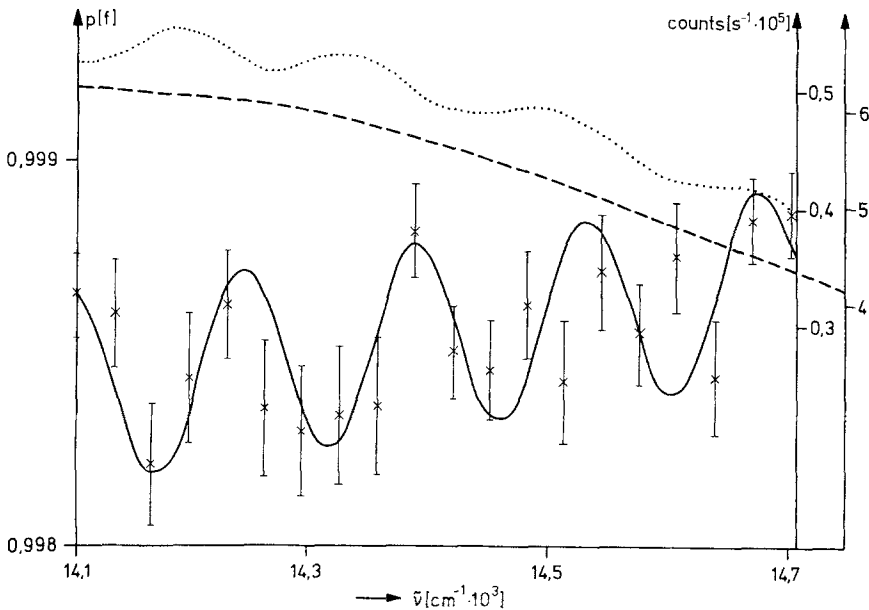


Fig. 1. Dynamic fluctuations $p[f]$ (—) of the emitted photon flux measured in a small region of $\Gamma_4(^3T_{1u}) \rightarrow \Gamma_1(^1A_{1g})$ transition of a microcrystalline Cs_2TeBr_6 sample at 10 K. Luminescence spectra recorded by usual photon counting emission spectroscopy at 2 K (····) and 10 K (----)

at room temperature being assigned to the e_g mode of the complex octahedron. The same interval is obtained from a 2 K luminescence spectrum recorded by usual emission spectroscopy (compare the spectra in Fig. 1).

Although only preliminary experiments could be carried out until now it can be concluded that the new technique measuring photon flux fluctuations may turn out to be a useful tool for obtaining the vibronic fine structure of electronic transitions which for solid state materials could not be resolved by usual emission spectroscopy. Moreover, by testing the new theory on various systems it is hoped to learn somewhat more about the coupling of the "well-defined" system with its environment.

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