On Optical Dispersion in Transparent Molecular Systems

I. Mössbauer Resonance Observation of a New Kind of Isomeric Molecular States Generated by Polarized Light

Ulrich Hauser, Volker Oestreich, and Heinz Dieter Rohrweck
Physikalisches Institut, Universität zu Köln, Köln, Germany

Received September 17, 1976

In a "crossed photon beams" experiment the action of light in a transparent medium is studied by Mössbauer resonance. Using cooled, temperature stabilized targets such as sodium nitroprusside, olivine and glasses, containing iron, no change of the hyperfine spectrum was observed by illumination with normal incoherent light of low intensity within the region of normal dispersion in agreement with the theory of optical dispersion.

There was, however, no agreement with theoretical expectation when sodium nitroprusside (whose structure is, therefore, reviewed in detail under the aspects of dispersion) was irradiated by laser light with otherwise unchanged experimental conditions, as intensity and range of wavelengths. A new kind of molecular state, producable only by polarized light, was observed. Its radiative lifetime is practically infinite, but it is thermally instable at elevated temperatures. The Mössbauer spectrum reveals a quadrupole splitting $\Delta E_Q = (+)(2.7357 \pm 0.0040)$ mm/s and an isomer shift $\delta = -(0.183 \pm 0.006)$ mm/s (relative to Fe(Pd)) at 100 K, markedly different from the normal groundstate. In the new state the axial symmetry, the sign of the $z$-component, and the three principal tensor axes of the electric field gradient at the Fe central atom coincide within the experimental limits of error with those of the groundstate.

I. Introduction

This paper is the first one of a series of investigations of the dispersive actions of polarized light on transparent Mössbauer substances. The experimental results obtained turn out to be non-trivial when considered by both the well-known optical processes described by dispersion theory and the well-known molecular structure of the substance used.

The variety of phenomena associated with the elastic and inelastic scattering of light by atoms, being free or bound in molecules or solids, are fundamentally described by the quantum theory of dispersion, i.e. the Kramers-Heisenberg formula [1]. If the finite width of the excited states, i.e. radiation damping, is taken into account by the theory then the generalized formulation of dispersion also includes resonance scattering and absorption. Although there is no doubt about the validity of the theory, it is, nevertheless, worthwhile to note that dispersion has never been investigated experimentally by a test probe which is an internal, microscopic part of the scattering target.

In the usual way optical dispersion is measured via correlations between the primary and secondary beam in terms of the intensity, the frequencies, the polarizations, the scattering angle, and of the orientation of the target if this possesses optical anisotropy. It is, however, also feasible to measure internally the action of the radiation field via the reaction of the interacting atoms which thus act simultaneously as test probes. Such an experiment should be viewed as a study of the basic dispersive processes in relation to the properties of the target rather than the other way around. Possible test probes are represented e.g. by Mössbauer nuclei if they are regular constituents of a transparent medium.

In the paper we report on a "crossed photon beams" experiment on optical dispersion. The target is a transparent single crystal whose properties are known as thoroughly as possible and which contains Mössbauer nuclei located at regular lattice sites. If this crystal is irradiated by a light beam, in particular by
the coherent, polarized light of a cw laser, we measure
"simultaneously" the action of the optical radiation
field on the Mössbauer nuclei by transmitting a Möss-
bauer resonance beam through the crystal.
In Section II we discuss in general the conditions for
such an experiment and the possible observable effects
of light on a Mössbauer nucleus as predicted by usual
dispersion theory. In Section III we apply these con-
siderations to the substance investigated especially:
sodium nitroprusside, Na$_2$Fe(CN)$_5$NO·2H$_2$O. It is
necessary to do this in detail in view of the peculiar
experimental results obtained. The experimental meth-
od and details are described in Section IV. First ex-
perimental results, being in contrast with conven-
tional expectation, are presented in Section V.

II. General Considerations

Any observable action of an optical radiation field on
a Mössbauer nucleus must be caused by a change of
the parameters which determine the Mössbauer
hyperfine spectrum. It is, therefore, expedient to out-
line briefly what can be expected from dispersion
theory. Before doing so, however, we should state the
experimental limitations.

1. Since optical light scattering and Mössbauer tran-
sitions within the target are statistically independent,
the notion "simultaneous" used above can merely be
understood as a random coincidence of light and
gamma quanta within a reasonable resolution time
to be defined as long as non-linear effects can be
neglected. In all cases the observability of a change of
the Mössbauer spectrum will depend sensitively upon
the intensities of the optical and Mössbauer radiation.
These intensities, however, are limited experimentally:
on the one hand the intensity of the Mössbauer radia-
tion is limited due to the single quantum counting
technique, on the other hand the light intensity is
limited by processes which transfer energy to the
target. The latter processes will cause a gradual
heating-up of the crystal or even its destruction. Thus,
the regions of anomalous dispersion, i.e. optical
resonance absorption, have to be avoided when
choosing the laser frequencies. Nevertheless, even in
the region of normal dispersion there will be energy
transfer owing to inelastic scattering and faint ab-
sorptive processes.

2. Let us now discuss in brief the possible effects which
could act on a Mössbauer nucleus due to the presence
of an optical radiation field. Elastic scattering of light
will, at least in isotropic substances, give no contri-
bution to a Mössbauer spectrum. Classically the time
average of the dynamic charge polarization which
oscillates with the frequency of the optical radiation
field will be zero when related to the mean lifetime of a
Mössbauer state. Thus, the isomer shift of a Möss-
bauer spectrum determined by the electronic charge
density at the Mössbauer nucleus will not be changed,
if the target temperature is kept constant.
A new, additional Mössbauer hyperfine pattern, dif-
f ering from the normal groundstate spectrum by a
different hyperfine splitting and a different isomer
shift, can only be expected if dispersive optical proces-

ses lead to a final excited state whose lifetime is com-
parable to or longer than that of the Mössbauer state.
Such a state with such a long lifetime must differ from
the groundstate by its electronic quantum numbers
since they determine the nature of its retarded or
forbidden decay probability. Thus, one expects in
terms of dispersion theory [1], that the matrix elements
describing the virtual excitation and deexcitation of
intermediate states will be given by electronic transi-
tions. Vibrational transitions, however, being super-
imposed upon electronic transitions should give no
contribution to the change of a Mössbauer spectrum
due to the short lifetime of these excited states.
Certainly there should be contributions from scatter-
ing transitions of a multipole order higher than dipolar
and also from non-linear optical effects in solids [2]
extensively studied in recent years by standard
methods. However, as emphasized above, the necessity
for a Mössbauer target of finite geometric extension
forbids the irradiation by very intense cw laser beams,
and therefore non-linear contributions will not be
observable by us.
It should be noted that other possible effects due to
light irradiation of non-transparent Mössbauer targets
have been discussed previously. This concerns the
possibility of a gamma-optical two-quantum absorp-
tion process where, in addition to the Mössbauer
quantum, the optical photon, too, is in resonance [3].
Further, there was a search for and the observation of
changes of Mössbauer spectra induced by electronic
shell vacancies which were generated by ionizing
radiation of short wavelengths [4].

3. In agreement with the arguments given above we
in fact did not observe (with the experimental arrange-
ment described in Sect. IV) a detectable change of the
Mössbauer hyperfine spectra when using transparent
targets as e.g. glasses which contain Fe atoms or single
crystals of olivine, (Mg,Fe)SiO$_4$, which were irra-
diated by laser light within the region of normal
dispersion.
On the other hand we did observe a drastic change of
the Mössbauer spectrum when using sodium nitro-
prusside as a target. These changes occur already at
relatively low laser light intensities and within a