Combined Nuclear-Molecular Resonance Inelastic Scattering of X Rays

V.G. Kohn,¹ A. I. Chumakov,^{2,1,*} and R. Rüffer²

¹Russian Research Center "Kurchatov Institute," 123182, Moscow, Russia ²European Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France (Received 12 March 2004; published 15 June 2004)

We report on theoretical and experimental studies of nuclear inelastic scattering in a molecular crystal, whose atoms experience both molecular and lattice vibrations. In this case scattering proceeds as combined nuclear-molecular resonance inelastic scattering. The lattice vibrations give rise to inelastic scattering around the molecular resonances with an energy dependence identical to that around the nuclear resonance. The incoherent nature of the scattering in the molecular resonances results in a proper balance of elastic and inelastic components, which has important implications for studies of heterogeneous systems.

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The frequency spectrum of atomic vibrations in a molecule consists of well isolated resonances. The spectroscopy of these molecular resonances is a traditional field of several techniques as infrared absorption, Raman, and inelastic neutron scattering. Recently, these methods were complemented by the resonant nuclear inelastic scattering [1-4]. It proceeds via excitation of nuclear resonances, and allows one to probe vibrational dynamics of selected atoms with Mössbauer nuclei. The energy resolution of this new technique ($\sim 0.5 \text{ meV}$) is comparable with the linewidth of the molecular resonances.

In molecular crystals, the molecular resonances coexist with other vibrational modes, i.e., collective lattice phonons. In this Letter, we show a possibility to measure the density of states (DOS) of the lattice phonons around combined nuclear-molecular resonances. The idea is illustrated by Fig. 1. Conventional nuclear inelastic scattering occurs around the narrow nuclear resonance, where the frequency of incident radiation ω_{in} is equal to the sum of the nuclear resonance frequency ω_0 and the lattice phonon frequency ω . We demonstrate that, around the frequency of the double nuclear-molecular resonance $\omega_0 + \omega_i$, a similar phenomenon occurs, which we define as the combined nuclear-molecular inelastic scattering. Once this is understood, it is intuitively clear that the energy dependence of inelastic scattering (caused by lattice vibrations) around the combined nuclear-molecular resonance is identical to that around the main nuclear resonance. We show that this is, indeed, the case, provided the frequency of the molecular resonance is well beyond the frequencies of lattice vibrations.

The extraction of the DOS from the measured probability of nuclear inelastic scattering is based on the theory of incoherent scattering [5–7]. The theory properly describes the experimental data except for the central peak. According to the incoherent theory, the weight of the elastic peak must be equal to the Lamb-Mössbauer factor, i.e., the probability of nuclear scattering without recoil. In practice, however, the weight of the elastic peak is suppressed by coherent forward scattering. Therefore, one

cannot normalize the experimental data, assuming that the integral probability of scattering is equal to unity. To overcome the problem, the experimental data have to be normalized by the free nucleus recoil frequency $\omega_R =$ $\hbar k^2/2M_R$ using Lipkin sum rules [2,8,9]. Here k is the wave number of the incident photon, M_R is a mass of the resonant atom, and \hbar is the Planck constant. This way of normalization requires measurements of inelastic scattering in the entire energy range including all highfrequency molecular resonances even if one is interested in the phonon spectrum of lattice vibrations only.

Different from that, combined nuclear-molecular inelastic scattering is entirely consistent with the theory of incoherent scattering. This is a qualitative advantage, though quantitatively the intensity of the combined scattering is lower. As we show below, the weight of the molecular peak is closely proportional to the Lamb-Mössbauer factor f. Furthermore, the relative weight of inelastic processes with creation and annihilation of the lattice phonons is close to 1 - f. Therefore, the total scattering probability around any molecular peak is independent of the Lamb-Mössbauer factor.

These properties have important implications for studies of heterogeneous systems. Consider a phase transition



FIG. 1. Scheme of nuclear inelastic scattering (left) and combined nuclear-molecular inelastic scattering (right). Here ω_0 and ω_i are the frequencies of nuclear and molecular resonances, respectively; ω is the phonon frequency, ω_{in} is the incident photon frequency, and S is the probability of scattering in an arbitrary scale.

accompanied by a change of molecular frequencies. This is, for instance, a common case for spin crossover compounds [10], where coexisting phases differ in both lattice and molecular dynamics. Around the main nuclear resonance, inelastic scattering from various phases is superimposed, and their DOS cannot be separated. In the combined resonances, the lattice phonons of each phase contributes around its specific molecular resonances. Therefore, in principle, one can determine the lattice DOS for each coexisting phase separately.

Besides the DOS, several further properties of each phase can be derived using the sum rules. For example, the integral probability of nuclear scattering around the molecular resonance is not affected by lattice dynamics. Therefore, it can be used to monitor the concentration of that phase, which possesses this particular molecular mode. Furthermore, the relative area of the molecular peak in combined nuclear-molecular scattering gives the Lamb-Mössbauer factor of the corresponding phase.

Thus, combined nuclear-molecular scattering allows one to determine independently both the concentration and the Lamb-Mössbauer factor for each of the coexisting phases. This is not the case, for instance, for Mössbauer spectroscopy and nuclear forward scattering, where the Lamb-Mössbauer factor and concentration always enter as a product and, therefore, cannot be separated.

To lay the theoretical basis, we consider only one phase and, for simplicity, assume identical vibrational properties for all atoms with resonant nuclei. Neglecting the narrow width of the nuclear transition, the frequency dependence of the normalized probability density of nuclear scattering $S(\mathbf{k}, \omega)$ is given by the Fourier transformation of the intermediate self-correlation function $F(\mathbf{k}, t)$ [5–7,11]:

$$S(\mathbf{k},\omega) = \int \frac{dt}{2\pi} \exp(-i\omega t) F(\mathbf{k},t).$$
(1)

Here ω is the frequency shift of the incident x-ray photon from the frequency ω_0 of the nuclear resonance, and **k** is the wave vector of the incident photon. The function $F(\mathbf{k}, t) = \langle \exp[-i\mathbf{k}\mathbf{u}(0)]\exp[i\mathbf{k}\mathbf{u}(t)] \rangle$ describes the correlation of nuclear positions **u** in two moments separated by the time interval t. The angular brackets denote both quantum-mechanic and thermodynamic averaging.

The position of the resonant atom in the molecular crystal varies due to both lattice and molecular vibrations. We select a number of molecular resonances with frequencies beyond those of the lattice phonons. Assuming that there is no correlation between the lattice and molecular motions, the self-correlation function can be written as a product of the lattice and the molecular parts: $F(\mathbf{k}, t) = F_l(\mathbf{k}, t)F_m(\mathbf{k}, t)$. The two parts are related to the corresponding densities of states $g_l(\mathbf{k}, \omega)$ and $g_m(\mathbf{k}, \omega)$ of the lattice and molecular vibrations as

$$F_i(\mathbf{k}, t) = f_i(\mathbf{k}) \exp(M_i(\mathbf{k}, t)),$$

$$f_i(\mathbf{k}) = \exp(-M_i(\mathbf{k}, 0)),$$
(2)

where

$$M_i(\mathbf{k}, t) = \int d\omega \, \exp(i\omega t) \frac{\omega_R g_i(\mathbf{k}, |\omega|)}{\omega[1 - \exp(-\beta\omega)]}.$$
 (3)

Here i = l, m; f_l and f_m are, respectively, the lattice and molecular parts of the total Lamb-Mössbauer factor $f = f_l f_m$, $\beta = \hbar/k_B T$; T is the temperature, and k_B is the Boltzmann constant. The sum $g_l(\mathbf{k}, \omega) + g_m(\mathbf{k}, \omega)$ is normalized to unity.

We do not make special assumptions about the lattice part of the DOS $g_l(\mathbf{k}, \boldsymbol{\omega})$. In general, it contains all lowfrequency modes. The frequencies $\boldsymbol{\omega}_j$ for the intramolecular vibrations and the polarization vector \mathbf{e}_j for the resonant atom can be calculated for a single molecule in harmonic approximation (see, for example, [12,13]). We introduce the finite linewidth of the molecular resonance γ_j as a parameter to be determined from experimental data. Finally, we formally write the molecular part of DOS as

$$g_m(\mathbf{k},\,\boldsymbol{\omega}) = \sum_j W_j p_j(\boldsymbol{\omega} - \boldsymbol{\omega}_j),\tag{4}$$

where

$$W_j = \left(\frac{\mathbf{k}}{k} \cdot \mathbf{e}_j\right)^2, \qquad p_j(\omega) = \frac{\gamma_j}{\pi(\omega^2 + \gamma_j^2)}.$$
 (5)

To shorten, we omit the **k** argument in the formulas below. The parameter γ_j determines the linewidth only for single-phonon scattering. Such scattering dominates if $\omega_j \gg \omega_R$. Multiphonon contributions can also be calculated (see, for example, [13]). However, we can neglect them here because $|M_m(t)| \ll 1$. Indeed, for most of the Mössbauer nuclei, ω_R is much smaller than the frequencies of molecular resonances ω_j . Therefore, developing $\exp(M_m(t))$ we keep only the linear term.

For the same reason of shortness, we consider here only the Stokes ($\omega_j > 0$) part of the combined nuclearmolecular resonance. The analysis of the anti-Stokes part ($\omega_j < 0$) leads to similar expressions. That part, however, has a noticeable contribution only at very high temperatures.

Taking into account these remarks and using Eqs. (2)–(5), after a simple calculation we arrive at the following approximation for the self-correlation function:

$$F(t) \approx f \exp(M_l(t)) \left[1 + \sum_j \tilde{W}_j \exp(i\omega_j t - \gamma_j |t|) \right], \quad (6)$$

where

$$\tilde{W}_{j} = \frac{\omega_{R}W_{j}}{\omega_{j}[1 - \exp(-\beta\omega_{j})]}.$$
(7)

The first term (unity) in square brackets of Eq. (6) describes lattice dynamics alone, whereas other terms take into account molecular vibrations as well. Evaluating the Fourier transformation in Eq. (1) for the

243001-2

pure lattice part of the correlation function, we arrive at the energy dependence of scattering around the main nuclear resonance $S_l(\omega)$. Here we obtain the elastic peak replacing $\exp(M_l(t))$ by unity. The inelastic part of scattering $S_{li}(\omega)$ is obtained replacing $\exp(M_l(t))$ by the complementary term $A_l(t) = \exp(M_l(t)) - 1$:

$$S_{li}(\omega) = f \int \frac{dt}{2\pi} \exp(-i\omega t) [\exp(M_l(t)) - 1]. \quad (8)$$

The energy dependence of nuclear scattering around the *j*th molecular resonance $S_{mj}(\omega)$ can be obtained according to the same procedure. To simplify the calculation, we note that $A_l(t)$ has a maximum at t = 0 and varies with time much faster than $\exp(-\gamma_j |t|)$. Therefore, integrating the product of these two terms we set $\gamma_j = 0$. Then we arrive at the final expression for the frequency dependence of nuclear inelastic scattering:

$$S(\omega) = S_l(\omega) + \sum_j S_{mj}(\omega - \omega_j), \qquad (9)$$

where

$$S_l(\omega) = f\delta(\omega) + S_{li}(\omega), \qquad (10)$$

and

$$S_{mj}(\omega) = \tilde{W}_j[fp_j(\omega) + S_{li}(\omega)].$$
(11)

Equations (9)–(11) confirm our intuitive postulate: nuclear inelastic scattering around the combined nuclearmolecular resonance ($\omega \approx \omega_j$) is identical to that around the main nuclear resonance ($\omega \approx 0$). Both of them consist of a central peak weighted by the Lamb-Mössbauer factor f and the inelastic part. The inelastic part is related to the lattice vibrations and is identical in both cases. The width of the central peak is determined by the resonance lifetime, namely, by the nuclear lifetime for the main resonance (disregarded here), and by the molecular lifetime γ_j^{-1} for the combined resonance. The coefficient \tilde{W}_j gives the partial cross section of the combined nuclear-molecular resonant scattering for jth molecular resonance.

Integrating Eq. (8) over frequency, one finds that the inelastic fraction of scattering is equal to $(f_m - f)$, which is smaller than (1 - f). The difference, however, is negligible (e.g., ≤ 0.02 in the example below), because the molecular resonances do not contribute much to mean-square atomic displacements and, therefore, $f_m \approx 1$. Then, according to Eq. (11), the integral probability of nuclear scattering around the *j*th molecular resonance is $\tilde{W}_j f_m$. It is determined only by the molecular resonance parameters and does not depend on f_l . More generally, it is invariant under transformation of the crystal lattice. One can show that the validity of this conclusion is not affected by the used approximations.

In order to confirm the theoretical analysis, we measured the energy dependence of nuclear inelastic scattering in ferrocene (Fig. 2). The measurements were 243001-3 performed at the Nuclear Resonance beamline ID18 [14] of the European Synchrotron Radiation Facility with an energy resolution of 0.5 meV. The sharp peak of scattering at zero energy indicates the main nuclear resonance. Three narrow peaks at about 22, 59, and 61 meV are the molecular resonances of ferrocene, which involve displacements of the ⁵⁷Fe resonant atom [15]. Broad "pedestals" around the main and molecular resonances are related to inelastic scattering caused by lattice vibrations. The region around the high-frequency molecular resonances is shown in Fig. 3 in more detail. Note the slight shift and broadening of the molecular resonances with temperature.

An increase of temperature leads to the reduction of the elastic fraction of scattering f. In accordance with Eqs. (10) and (11), this causes a suppression of the scattering in the main and molecular resonances at the expense of the enhancing contribution of inelastic scattering related to the lattice modes. Figure 2 shows that inelastic scattering around the molecular resonances



FIG. 2. Energy dependence of nuclear inelastic scattering in ferrocene powder at various temperatures. Thin lines are to guide the eye.



FIG. 3. Energy dependence of nuclear inelastic scattering around the combined resonances. Thin lines are to guide the eye. Thick lines are obtained by the scaling of inelastic scattering around the main resonance (see text). The Lamb-Mössbauer factors are derived from the area of the normalized energy dependence of nuclear inelastic scattering in the entire energy range.

looks identical to that around the main resonance. To prove it, we scaled the energy dependence of inelastic scattering around the main resonance with the coefficients \tilde{W}_j [Eq. (7)] and compared the result to inelastic scattering around the molecular resonances without any adjustable parameter. The data for e_j^2 and ω_j were obtained from the derived DOS. Figure 3 shows that inelastic scattering around the molecular resonances is perfectly identical to that around the main resonance.

As discussed above, the relative weight of the molecular peaks in combined nuclear-molecular scattering gives the Lamb-Mössbauer factor f. We estimated the relative area of the molecular peaks in the 45-75 meV range (Fig. 3) and obtained f = 0.83, 0.59, 0.32, and 0.10 for T = 23, 72, 144, and 296 K, respectively. Within theerror bars, these values coincide with the Lamb-Mössbauer factors determined from the area of the normalized energy dependence of nuclear inelastic scattering in the entire energy range (as quoted in Fig. 3). Finally, we checked whether the integral probability of combined nuclear-molecular scattering is independent of the Lamb-Mössbauer factor f. We calculated the total area of normalized probability of nuclear scattering in the 45-75 meV range (Fig. 3) and obtained 1.53%, 1.48%, 1.5%, 1.75% for the above-mentioned temperatures. Within statistical accuracy, it stays constant in the entire temperature range despite an almost complete redistribution of the scattering probability between elastic and inelastic fractions.

In conclusion, we present a theoretical analysis and experimental measurements of combined nuclear-molecular resonant inelastic scattering. It proceeds around the energies of double nuclear-molecular resonances, and its energy dependence is determined by lattice vibrations identically to that around the main nuclear resonance. The properties of combined nuclear-molecular inelastic scattering have important implications for studies of heterogeneous systems. Because of the "assignment" to specific molecular resonances, it allows one to investigate lattice vibrations separately for the coexisting phases with different molecular modes.

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Note added.—While preparing this Letter for publication, we found that similar effects were considered (though not observed) in inelastic neutron scattering as well [16].

*Corresponding author.

Email address: chumakov@esrf.fr

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