# Raman, non-Raman, and anti-Raman dispersion in resonant x-ray scattering spectra of molecules

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The character of Raman dispersion is investigated for radiative and nonradiative resonant x-ray scattering of systems with vibrational degrees of freedom. It is shown that the center of gravity of the resonantly scattered x-rays and electrons of such systems is strongly dependent on frequency and spectral shape of the incoming x-ray radiation and on the parameters defining the potential surfaces of the states involved in the scattering event. Contrary to nonresonant x-ray and Auger emission, narrow band resonant excitation leads to a strong nonlinear dependence of the center of gravity, with an asymmetrical frequency dependence for this quantity. Contrary to atomic systems it is shown that resonant x-ray scattering of molecules often is guided by an anti-Raman dispersion law. [S1050-2947(96)09611-4]

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## I. INTRODUCTION

Many of the general aspects of radiative and nonradiative resonant x-ray scattering (RXS) are by now quite well understood on an electronic structure level of theory, see, e.g., Refs. [1–7]. The experimental progress in this field using synchrotron radiation and high-resolution spectrometers [8–12] has advanced to a point where the vibrational band shapes and even individual vibronic transitions can be studied. The situation for RXS thus matches the situation some 20 years ago for nonresonant x-ray [13] and Auger [14] emission, when vibrational structure was resolved in these spectroscopies. However, the manifestation of vibrational structure and of the nuclear dynamics is qualitatively very different between the resonant and nonresonant spectroscopies. This goes not only for the build-up of the Franck-Condon envelopes and for the special electronic interference effects, but most important is the (nonadiabatic) vibronic coupling between resonant core-excited states of different symmetries that influences the RXS spectral shape quite significantly [15–17] and that is strongly frequency dependent [17,18].

In the present work we investigate yet another feature of resonant radiative or nonradiative emission, with no counterpart in the nonresonant case, namely, the Raman dispersion of energies of the scattered particles, more precisely how this dispersion is manifested in molecules. Like other ‘‘Raman’’ related effects, such as resonance narrowing [19,2] and Stokes doubling [3,20,6], the Raman dispersion [19,2] has been predicted and firmly established by observations in atomic systems [1,12,11]. In contrast to atomic systems, for which the Raman dispersion in general is linear (for inelastic scattering with narrow band excitation), the presence of vibrational degrees of freedom and closeness of many vibrational sublevels make the energy dispersion of the scattered particle a complicated function of the exciting photon energy. In molecules there is thus a strong complication of the RXS spectral shape by the vibrational structure, and it is convenient to study only a few quantities characterizing the spectral band that can be determined by experiment; here we focus on the center of gravity (CG) of the emission bands. The main aim of our paper is thus to investigate how these quantities depend on the frequency and spectral distribution of exciting radiation and on the potential surfaces of the electronic states involved in the RXS process.

The strong dependence of the RXS spectral shape on the spectral function of the exciting radiation has previously been postulated [3,20,6,11]. The numerical experiment by Armen and Wang [6] demonstrated the nonlinear dispersion of the peak maxima and how the full width at half maximum (FWHM) of the RXS resonances developed in the framework of a three-level, atomic model. Cederbaum and Tarantelli [5] used a time-dependent ansatz to investigate the first two moments (CG and band width) of the nonresonant x-ray emission complicated by vibrational structure. Since the spectral distribution in Ref. [5] was assumed to be constant the center of gravity and the width of nonresonant emission bands did not depend on the frequency of the exciting x-ray photon. Taking into account results from the investigation of peak maxima dispersion [6] one can expect that also the center of gravity of RXS will depend on $\omega$ in a nonlinear way.

The paper is organized as follows. A general time-independent description of the CG is given in Sec. II. To understand the main spectral features of the CG and the second moment of RXS bands a three-level model is considered in Sec. III. We show here that the spectral dependence of CG in this three-level system reminds one qualitatively of the dispersion of the peak maxima [6], except for the region where Stokes doubling operates [3,20,6,11]. Contrary to peak maxima and widths (FWHMs) the spectral dependence of the CG and the second moment can be given a fully analytical description. The following sections are devoted to the investigation of the center of gravity of RXS signals for electronic-vibrational (vibronic) transitions in the framework of the harmonic approximation. In Sec. IV A we reproduce by means of a time-independent approach the result in Ref. [5] for broad band excitation. We show that the Raman dispersion of CG appears in this case only for tail excitation. The narrow band excitation investigated in the following section (Sec. IV C) demonstrates the strong nonlinear char-

acter of the CG dispersion. In particular, the frequency dependence of the center of gravity shows oscillatory behavior if the incoming photon frequency $\omega$ is within the frequency range given by the absorption band and if the lifetime broadening is small in comparison with vibrational frequencies. These oscillations are quenched when the lifetime broadening increases. All parameters for the CG are expressed through the lifetime broadening, the vibrational frequencies, and the equilibrium distances of the states involved in the RXS process. A time-dependent approach (Sec. IV C 1) demonstrates the strong influence of nuclear dynamics on the asymptotic behaviour of the CG. Our findings are summarized in the last section, Sec. V.

## II. CENTER OF GRAVITY OF RXS BANDS

We consider in the following a RXS process taking place in a diatomic molecule. This does not limit the generality for the approach and the obtained results, but allows for crucial simplifications in notation and tractability of expressions. For ordinary temperatures the diatomic molecule is assumed initially to be in the lowest vibrational level $\omega_o/2$ (vibrational wave function $|o\rangle$) of the ground state ($o$). By absorbing incoming x-ray photons with frequency $\omega$ the molecule is excited to the vibrational level $\omega_i(m+\frac{1}{2})$ of the intermediate electronic state ($i$) with the vibrational wave function $|m\rangle$. Nuclear dynamics will be considered in the harmonic approximation. Due to the vacuum fluctuations this intermediate state decays emitting x-ray photons with the frequency $\omega'$ to the vibrational level $\omega_f(n+\frac{1}{2})$ with the wave function $|n\rangle$ of the final electronic state ($f$). Except for this radiative scattering channel, the core excited state can decay, nonradiatively emitting an Auger electron. The vibrational problem in radiative and nonradiative RXS is essentially the same and both cases are covered by the theory presented below. The spectral properties of RXS are guided by the double differential cross section [3]

$$\sigma(\omega,\omega') = \sum_n |F_f|^2 \Phi(\omega'+\omega_{fo}-\omega,\gamma), \qquad (1)$$

convoluted with the unit normalized spectral function of the excitation radiation $\Phi$ centered at frequency $\omega$ and having the width $\gamma$. We will use here atomic units and the notation $\sigma(\omega,\omega')$ for the double differential cross section. $\omega_{ij}$ denotes the frequency for a resonant transition between molecular states $i$ and $j$:

$$\omega_{ij} = E_i(R_i) + \frac{\omega_i}{2}(n_i+\tfrac{1}{2}) - E_j(R_j) - \frac{\omega_j}{2}(n_j+\tfrac{1}{2}). \quad (2)$$

Here $E_i(R_i)$ is the electronic energy of the $i$th state at the equilibrium geometry $R_i$. In the following we let $o$, $m$, $n$ denote vibrational quantum numbers of the ground, intermediate, and final states, respectively.

The scattering amplitude $F_f$ is given by the Kramers-Heisenberg formula. According to the Franck-Condon principle the RXS amplitude can be written as [3,21,22]

$$F_f = \sum_m \frac{\langle n|m\rangle\langle m|o\rangle}{\omega'-\omega_{if}+i\Gamma}, \qquad (3)$$

where $\Gamma$ is the lifetime broadening [half width at half maximum (HWHM)]. For the sake of transparency we have dropped the nonessential constant multipliers on the right-hand sides of Eqs. (1) and (3).

The position of the vibrational band in the RXS spectrum is given by the center of gravity (CG) of the band:

$$\epsilon(\omega) = \frac{\sigma_1(\omega)}{\sigma_o(\omega)}. \qquad (4)$$

The CG is expressed through the zero $\sigma_o(\omega)$ and first $\sigma_1(\omega)$ and moments of the RXS cross section (1):

$$\sigma_1(\omega) = \int d\omega'\, \omega'\, \sigma(\omega,\omega') = \mathrm{Re} \sum_{n=0}^{\infty} \sum_{m,m_1=0}^{\infty} \int_{-\infty}^{\infty} \frac{\langle o|m_1\rangle\langle m_1|n\rangle\langle n|m\rangle\langle m|o\rangle(\xi+\omega-\omega_{fo})}{(\xi+\omega-\omega_{i_1o}-i\Gamma)(\xi+\omega-\omega_{io}+i\Gamma)}\,\Phi(\xi,\gamma)d\xi. \qquad (5)$$

The area of the emission band $\sigma_o(\omega)$ has an important property, namely, that the interference contribution to the zero moment is equal to zero [23]. This means that the integral RXS cross section for a given electron transition

$$\sigma_o(\omega) = \int d\omega'\, \sigma(\omega,\omega')$$

$$= \sum_{m=0}^{\infty} |\langle m|o\rangle|^2 \int_{-\infty}^{\infty} \frac{\Phi(\xi,\gamma)}{(\xi+\omega-\omega_{io})^2+\Gamma^2}\, d\xi \qquad (6)$$

coincides with the absorption cross section. As one can see from Eqs. (4) and (5) the CG depends strongly on the frequency of excited radiation $\omega$ and on the spectral function $\Phi$.

To see this in detail we consider two cases important in applications: broad band excitation and narrow band excitation.

## III. THREE-LEVEL MODEL

To start we would like to understand the general properties of the frequency dependence of the CG. To do this we neglect for a moment the vibrational structure of the electronic states $o$, $i$, and $f$ and consider RXS for a three-level molecule with levels $o$, $i$, and $f$ (Fig. 1). It is convenient to present CG in the following form:

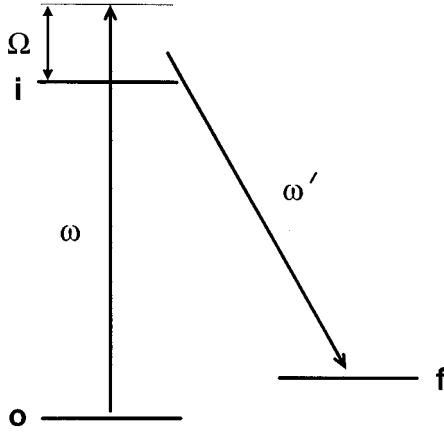$$\epsilon(\omega) = \omega_{if} + \varphi(\Omega), \qquad (7)$$
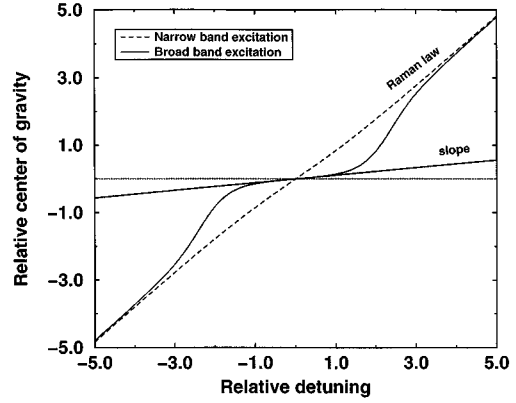
FIG. 1. Three-level model for RXS.



FIG. 2. The dispersion of center of gravity (7), (8) for the three-level model. The relative CG and relative detunings are $[\epsilon(\omega) - \omega_{if}]/\gamma$ and $\Omega/\gamma$. The broad band case was calculated according to Eq. (8) for $\Gamma/\gamma = 0.1$, while the narrow-band excitation was calculated for $\Gamma/\gamma = 2$. The dispersion of CG for a frequency independent spectral function ($\gamma = \infty$) is depicted by a dotted line. The slope of CG under broad band excitation was calculated according to Eq. (11).

where $\Omega = \omega - \omega_{io}$ is the detuning of incoming photon frequency $\omega$ relative to the absorption resonant frequency $\omega_{io}$. We will see below that the resonant frequency $\omega_{if}$ of emission transition $i \to f$ has the meaning of the center of gravity for broad band excitation ($\gamma/\Gamma \to \infty$). The function $\varphi(\Omega)$ describes the deviation of exact CG $\epsilon(\omega)$ from $\omega_{if}$ for broad band excitation and is defined by the following equation:

$$\varphi(\Omega) = \Omega + \frac{\displaystyle\int_{-\infty}^{\infty} d\xi \frac{\xi \Phi(\xi, \gamma)}{(\xi + \Omega)^2 + \Gamma^2}}{\displaystyle\int_{-\infty}^{\infty} d\xi \frac{\Phi(\xi, \gamma)}{(\xi + \Omega)^2 + \Gamma^2}}$$

$$= \Omega + \gamma \frac{\mathrm{Re}[zw(z)]}{\mathrm{Re}[w(z)]}. \qquad (8)$$

Here $z = (i\Gamma - \Omega)/\gamma$. This function is antisymmetric: $\varphi(-\Omega) = -\varphi(\Omega)$ (Fig. 2). As the most important limiting case we approximated in Eq. (8) the spectral function of incoming x-ray photons by a Gaussian: $\Phi(\Omega, \gamma) \propto \exp[-(\Omega/\gamma)^2]$. Properties of the error function for a complex argument $w(z)$ [24] then yield the following asymptotic values for the $\varphi(\Omega)$ function:

$$\varphi(\Omega) = \Omega \begin{cases} \dfrac{2\Gamma}{\sqrt{\pi}\gamma} \simeq 0, & \text{if } \sqrt{\Omega^2 + \Gamma^2} \ll \gamma \\[3mm] 1 - \dfrac{\gamma^2}{\Omega^2 + \Gamma^2} \simeq 1, & \text{if } \sqrt{\Omega^2 + \Gamma^2} \gg \gamma. \end{cases} \qquad (9)$$

This allows us to understand the general spectral features of the center of gravity $\epsilon(\omega)$.

### A. Broad band excitation

We will refer to broad band excitation when the width of the spectral function is large in comparison with the lifetime broadening

$$\gamma \gg \Gamma. \qquad (10)$$

Contrary to intuition the CG depends on the frequency $\omega$ in this limiting case. Indeed, in accordance with Eqs. (7) and (9), this dependence is given as

$$\epsilon(\omega) = \begin{cases} \omega_{if} + \Omega \dfrac{2\Gamma}{\sqrt{\pi}\gamma} \simeq \omega_{if}, & \text{if } |\Omega| \ll \gamma \\[3mm] \omega_{if} + \Omega - \dfrac{\gamma^2}{\Omega}, \simeq \omega_{if} + \Omega, & \text{if } |\Omega| \gg \gamma. \end{cases} \qquad (11)$$

Equation (11) shows that the slope of $\epsilon(\omega)$ increases strongly from $2\Gamma/(\sqrt{\pi}\gamma)$ to 1 if $|\Omega|$ passes through $|\Omega| \sim \gamma$ (see solid lines in Fig. 2). When $|\Omega| < \gamma$, the center of gravity is very close to the resonant emission frequency $\omega_{if}$, and will follow the Raman law

$$\epsilon(\omega) = \omega_{if} + \Omega = \omega - \omega_{fo} \qquad (12)$$

if $|\Omega|$ considerably exceeds $\gamma$. The linear dispersion (12) is known as the Raman-Stokes or the Raman law. The center of gravity is independent on the frequency $\omega$ only if the spectral function $\Phi(\Omega, \gamma)$ is constant, $\gamma/\Gamma \to \infty$ (dotted line in Fig. 2).

### B. Narrow band excitation

The frequency dependence of CG is qualitatively different when x-ray fluorescence is induced by a narrow band x-ray beam

$$\gamma \ll \Gamma. \qquad (13)$$

In the considered limit CG follows the second equation (9) with the following asymptotic behavior:

$$\epsilon(\omega) = \omega_{if} + \Omega \left( 1 - \frac{\gamma^2}{\Omega^2 + \Gamma^2} \right)$$

$$= \omega_{if} + \begin{cases} \Omega \left[ 1 - \left( \dfrac{\gamma}{\Gamma} \right)^2 \right], & \text{if } |\Omega| \ll \Gamma \\[3mm] \Omega - \dfrac{\gamma^2}{\Omega}, & \text{if } |\Omega| \gg \Gamma. \end{cases} \qquad (14)$$
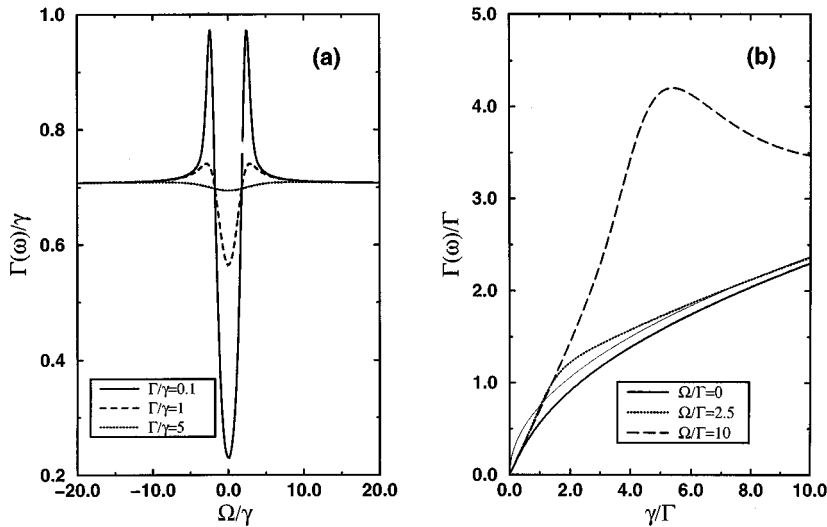
FIG. 3. The second moment [spectral width, $\Gamma(\omega)$] of RXS band for the three-level model. (a) The dispersion of $\Gamma(\omega)$. (b) The dependence of $\Gamma(\omega)$ (15) on spectral width $\gamma$ of incident radiation. A thin line shows the asymptote of $\Gamma(\omega)$ (17) for large $\gamma$ ($\gamma \gg \sqrt{\Omega^2 + \Gamma^2}$).

The slope of CG $\epsilon(\omega)$ increases slowly when the magnitude of detuning $|\Omega|$ increases. In the considered limit CG follows closely the Raman law (12) (dashed line, Fig. 2). So both broad band and narrow band excitations lead to the same result, namely, to the Raman law (12), when the incoming photon frequency is tuned sufficiently far from the x-ray absorption resonance $|\Omega| \gg \Gamma, \gamma$.

## C. Spectral width of RXS bands

The spectral width $\Gamma(\omega)$ of the emission band is the second important characteristic quantity of the RXS profile. This quantity can be introduced in two different ways. First, by defining $\Gamma(\omega)$ the FWHM of the spectral band [6]. Here we use the second alternative, namely, we define $\Gamma(\omega)$ as the second moment of the RXS profile

$$\Gamma(\omega) = \left( \int_{-\infty}^{\infty} d\omega' [\omega' - \epsilon(\omega)]^2 \frac{\sigma(\omega, \omega')}{\sigma_o(\omega)} \right)^{1/2}. \quad (15)$$

The main advantage of using the second moment compared to the FWHM is given by the simpler analytical properties of this quantity. The three-level model with a Gaussian spectral function $\Phi(\Omega, \gamma) \propto \exp[-(\Omega/\gamma)^2]$ allows to calculate the spectral width (15) explicitly as

$$\Gamma(\omega) = \left( \frac{\gamma \Gamma}{\sqrt{\pi} \, \mathrm{Re} \, w(z)} - \varphi^2(\Omega) - \Gamma^2 \right)^{1/2}. \quad (16)$$

The dependences of the second moment (16) on detuning and on width of the spectral function are depicted in Fig. 3. To understand the properties of $\Gamma(\omega)$ it is useful to consider the limiting cases of narrow band and broad band excitations. As for the CG we can use the properties of the $\varphi$ function and the error function for a complex argument. The following asymptots are then obtained:

$$\Gamma(\omega) = \begin{cases} \left( \dfrac{\gamma \Gamma}{\sqrt{\pi}} \right)^{1/2}, & \text{if } \sqrt{\Omega^2 + \Gamma^2} \ll \gamma \\[3mm] \dfrac{\gamma}{\sqrt{2}}, & \text{if } \sqrt{\Omega^2 + \Gamma^2} \gg \gamma. \end{cases} \quad (17)$$

For *broad band excitation* ($\sqrt{\Omega^2 + \Gamma^2} \ll \gamma$) the second moment of the RXS band diverges as $\sqrt{\gamma}$ when $\gamma$ tends to infinity (17). This divergency is caused by the slowly decaying Lorentzian tail of the scattering amplitude (3) [5]. Contrary to the second moment this divergency is absent for the FWHM. As is well known the FWHM tends to the lifetime broadening $2\Gamma$ for broad band excitation.

Going to the *narrow band excitation* ($\sqrt{\Omega^2 + \Gamma^2} \gg \gamma$), Eq. (17) and Fig. 3(a) show that $\Gamma(\omega)$ depends slowly on the detuning $\Omega$ and that $\Gamma(\omega)$ tends to zero as $\gamma/\sqrt{2}$ when $\gamma \to 0$. This is the basis for "resonance narrowing" of RXS spectroscopy when the spectral resolution goes below the lifetime broadening [19,2].

## IV. CENTER OF GRAVITY OF VIBRONICALLY BROADENED RXS RESONANCES

The presence of vibrational structure complicates the RXS cross section (1) quite considerably. The concept of moments of the cross section is very useful for the analysis of spectral features of RXS given by experiment and for receiving information on potential energy surfaces of states involved in the RXS process. In the spirit of the "atomic" three-level model we will calculate CG for a many-level system (Fig. 4) that simulates molecules, using the general Eqs.
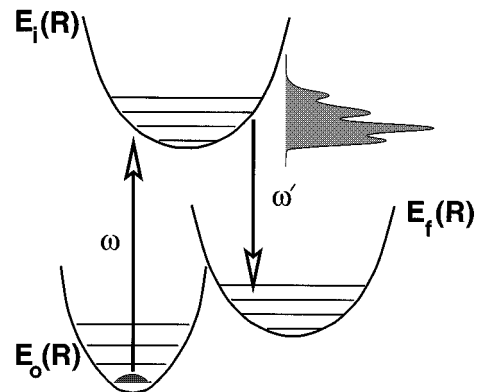


FIG. 4. Scheme for electronic and vibrational levels involved in RXS.

(4)–(6). Also, in this context we analyze the two important limiting cases of broad band and narrow band excitations.

### A. Broad band excitation

We first consider the case with a photon function having a large width $\gamma$

$$\gamma \gg \Gamma_{\text{eff}}, \quad |\omega - \omega_{io}|. \tag{18}$$

Here $\Gamma_{\text{eff}}$ is the effective width of the envelope formed by the vibronic transitions within the x-ray absorption resonance.

$$\epsilon(\omega) = 4\Gamma^2 \sum_{m,m_1=0}^{\infty} \frac{\langle o|m_1\rangle\langle m_1|(E_i(R_i) - E_f(R_f) + H_i - H_f)|m\rangle\langle m|o\rangle}{\omega_i^2(m-m_1)^2 + 4\Gamma^2}. \tag{20}$$

The vibrational Hamiltonians $H_i$ and $H_f$ of the electronic states $i$ and $f$ are connected with each other in the harmonic approximation by the equation

$$H_f = H_i + \tfrac{1}{2}\mu\omega_f^2(R_i - R_f)^2 + V,$$

$$V = \frac{\mu}{2}(\omega_f^2 - \omega_i^2)\xi^2 + \mu\omega_f^2(R_i - R_f)\xi, \tag{21}$$

where $\xi = R - R_i$ is the displacement from the equilibrium internuclear distance of the core excited state and $\mu$ is the reduced mass.

Taking into account Eq. (21) and the sum rules (44) one finally obtains the following expression for CG under broad band excitation (18)

$$\epsilon(\omega) = \epsilon_{if}^S + \epsilon_{if}^D. \tag{22}$$

Two qualitatively different terms

$$\epsilon_{if}^S = E_i(R_o) - E_f(R_o) + \frac{\omega_i^2 - \omega_f^2}{4\omega_o},$$

$$\epsilon_{if}^D = \frac{\omega_f^2 - \omega_i^2}{4\omega_i^2}\left(\mu\omega_i^2(R_o - R_i)^2 + \frac{\omega_i^2 - \omega_o^2}{2\omega_o}\right)\frac{\omega_i^2}{\omega_i^2 + \Gamma^2}$$

$$+ \mu\omega_f^2(R_o - R_i)(R_i - R_f)\frac{\omega_i^2}{\omega_i^2 + 4\Gamma^2} \tag{23}$$

contribute both to the center of gravity (22). The first term $\epsilon_{if}^S$ is due to the vertical or sudden transition, while the second one $\epsilon_{if}^D$ is purely of dynamical origin [5]. Indeed the dynamical contribution $\epsilon_{if}^D$ tends to zero when the core excited state is short-lived ($\Gamma \gg \omega_i$). Equations (22) and (23) were received first by Cederbaum and Tarantelli [5] in the framework of a time-dependent approach. Here we used the connection between the electronic energy $E_i(R)$ at the point $R$ and its equilibrium value $E_i(R_i)$: $E_i(R) = E_i(R_i)$

This condition allows us to consider the spectral function as constant $[\Phi(\omega' + \omega_{fo} - \omega, \gamma) = \text{const}]$. Thus, according to Eqs. (5) and (6) the center of gravity does not depend on the frequency $\omega$

$$\epsilon(\omega) = \text{const} \tag{19}$$

under broad-band excitation (18) [5]. According to Eq. (6) now $\sigma_o(\omega) = \pi\Phi/\Gamma$. Thus the center of gravity (4) reads

$+ \mu\omega_i^2(R - R_i)^2/2$. It is relevant to point out that $\epsilon_{io}^S$ defined by Eq. (23) is the center of gravity of the vibronic absorption band $o \to i$.

### B. Tail excitation

Let us now tune the incoming photon frequency $\omega$ far from the x-ray absorption resonance:

$$|\omega - \omega_{io}| \gg \gamma, \quad \Gamma, \quad \omega_o \tag{24}$$

in which case the x-ray photons core excite the molecule by the tails of the absorption line. For tail excitation (24) the denominators on the right-hand side of Eqs. (5) and (6) can be removed from the integrals over $\zeta$, and hence we obtain

$$\epsilon(\omega) = \sum_{n=0}^{\infty} \langle o|n\rangle(\omega - \omega_{fo})\langle n|o\rangle. \tag{25}$$

A method outlined in the preceding subsection leads to the Raman law

$$\epsilon(\omega) = \omega - \epsilon_{fo}^S. \tag{26}$$

A comparison with Eq. (23) shows that the frequency

$$\epsilon_{fo}^S = E_f(R_o) - E_o(R_o) + \frac{\omega_f^2 - \omega_o^2}{4\omega_o} \tag{27}$$

has the meaning of the center of gravity of a sudden or vertical "absorption transition" $o \to f$.

Comparing with the general expression for the RXS amplitude (3) one receives now a deeper interpretation of this result. Indeed, according to condition (24) the RXS amplitude is proportional to the overlap integral $\langle n|o\rangle$ between the ground- and final-state vibrational wave functions, which leads directly to the following result for the RXS amplitude:

$$F_f \propto \langle n|o\rangle. \tag{28}$$

Thus a sudden (vertical) transition from the initial $|o\rangle$ to the final $|f\rangle$ states takes place. This expression for $F_f$ coincides with the short lifetime limit ($\Gamma \to \infty$) [22].

The time-dependent representation for the RXS amplitude [4] leads to the same result (28) when the core excited state is short-lived ($1/\Gamma$ is small) or if the detuning $\Omega_o$ is large (see also Sec. IV C 1). Indeed, the wave packet excited from the ground state $|o\rangle$ at time $t=0$ decays to the final molecular state $|f\rangle$ at different times ($0 \le t \le \infty$). The partial RXS amplitude corresponding to the time $t$ is proportional to the phase factor $\exp(i\Omega_o t - \Gamma t)$. When the lifetime broadening or detuning $\Omega_o = \omega - \omega_{io}$ is large, only a partial amplitude of the sudden transition ($t=0$) gives a significant contribution to $F_f$. Indeed, the contributions of decay events at $t \ne 0$ are negligibly small due to the damping factor $\exp(-\Gamma t)$ if $\Gamma$ is large or when the $\exp(i\Omega_o t)$ factor oscillates strongly, as it does when the frequency is tuned far away from the absorption resonance. In the latter case the RXS process can also be considered as a sudden process because the interference suppression of the decay contributions to $F_f$ for different times $t$. The same effect is given also by the three-level model [see lower Eq. (11)]. So contrary to Eq. (22) the detuning of $\omega$ outside of absorption band $|\Omega| < \gamma$ restores the frequency dependence of CG according to the Raman law (26).

Figure 2 gives a qualitative summary of the results obtained in Secs. IV A and IV B. When the detuning from the absorption resonance is smaller than the width of the spectral function, $|\Omega| < \gamma$, the center of gravity (22) depends slowly on $\omega$ for broad band excitation. Strong frequency dependence appearing near $|\Omega| \sim \gamma$ tends to become linear (26) if $|\Omega| \gg \gamma$.

## C. Narrow band excitation

As it was shown for the three-level model (see Sec. III) the frequency dependence of the center of gravity under narrow band excitation

$$\gamma \ll \Gamma_{\text{eff}} \tag{29}$$

qualitatively differs from the case of broad band excitation. In this subsection we consider the corresponding narrow band case for a system with vibronic transitions. Since the spectral function now can be approximated by a $\delta$ function [$\Phi(\Omega, \gamma) \simeq \delta(\Omega)$] the area of the RXS band (6) associated with the particular electronic transition is given by

$$\sigma_o(\omega) = \sum_{m=0}^{\infty} \frac{|\langle m|o\rangle|^2}{(\Omega - m\omega_i)^2 + \Gamma^2}. \tag{30}$$

Here $\Omega = \omega - [E_i(R_i) - E_o(R_o) + (\omega_i - \omega_o)/2]$ is the detuning of incoming photon frequency from the resonant frequency of the adiabatic transition $o \to i$. This adiabatic frequency constitutes the lowest one for the absorption transition, and $\Omega$ has therefore also the meaning of a frequency of detuning from the bottom of the corresponding emission band.

In accordance with Eq. (2), the first moment (5) of the absorption cross section is changed to

$$\sigma_1(\omega) = \text{Re} \sum_{m,m_1=o}^{\infty} \frac{\langle o|m_1\rangle\langle m_1|\{\omega - [E_f(R_f) - E_o(R_o) - \frac{1}{2}\omega_o] - H_f\}|m\rangle\langle m|o\rangle}{(\Omega - m_1\omega_i - i\Gamma)(\Omega - m\omega_i + i\Gamma)}, \tag{31}$$

It is convenient to present $\epsilon(\omega)$ (4) relative to the frequency $\widetilde{\epsilon}_{if}^S$ of the sudden (or vertical) emission transition $i \to f$ from the lowest vibrational level ($m=0$) of the core excited state $i$: $\widetilde{\epsilon}_{if}^S = E_i(R_i) - E_f(R_i) + (\omega_i^2 - \omega_f^2)/(4\omega_i)$. The replacement of the final-state vibrational Hamiltonian $H_f$ by that of the core excited state $H_i$ (21) yields the following final result:

$$\epsilon(\omega) - \widetilde{\epsilon}_{if}^S = \Omega + \delta\epsilon(\omega),$$

$$\delta\epsilon(\omega) = -\Delta_+ f(\omega) - \Delta f_1(\omega) - \Delta_- f_2(\omega), \tag{32}$$

where

$$\Delta_{\pm} = \frac{\omega_f^2 \pm \omega_i^2}{2\omega_i}, \quad \Delta = \left(\frac{2\mu}{\omega_i}\right)^{1/2} \omega_f^2 (R_i - R_f). \tag{33}$$

The nonlinear frequency dependence of CG (32) originates entirely from the functions

$$f(\omega) = \frac{1}{\sigma_o(\omega)} \sum_{m=0}^{\infty} \frac{m|\langle m|o\rangle|^2}{(\Omega - m\omega_i)^2 + \Gamma^2},$$

$$f_1(\omega) = \frac{1}{\sigma_o(\omega)} \sum_{m=0}^{\infty} \frac{\sqrt{m+1}\langle o|m\rangle\langle m+1|o\rangle\{(\Omega - m\omega_i)[\Omega - (m+1)\omega_i] + \Gamma^2\}}{[(\Omega - m\omega_i)^2 + \Gamma^2]\{[\Omega - (m+1)\omega_i]^2 + \Gamma^2\}}, \tag{34}$$

$$f_2(\omega) = \frac{1}{\sigma_o(\omega)} \sum_{m=0}^{\infty} \frac{\sqrt{(m+1)(m+2)}\langle o|m\rangle\langle m+2|o\rangle\{(\Omega - m\omega_i)[\Omega - (m+2)\omega_i] + \Gamma^2\}}{[(\Omega - m\omega_i)^2 + \Gamma^2]\{[\Omega - (m+2)\omega_i]^2 + \Gamma^2\}}.$$
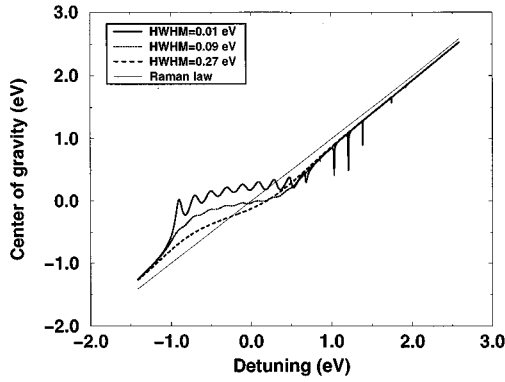
FIG. 5. Dependence of center of gravity on lifetime broadening for narrow band excitation (29). Input data correspond to O $K$ emission of the CO molecule (Table I).



FIG. 6. Influence of vibrational structure on CG slope. X-ray absorption profile is given for $\Gamma = 0.001$ eV. (a) Data for O $K$ emission of CO molecule (Table I). Slope (37) is positive. (b) Anti-Raman behavior ($\omega_f > \omega_i$). Input data are the same with (a) except $\omega_f = 0.23$ eV. Slope (37) is negative.

The typical frequency dependence of CG is shown in Fig. 5 for different lifetime broadenings $\Gamma$. The parameters used in these calculations correspond to oxygen $K$ emission of the CO molecule. Spectroscopic constants ($R_j, \omega_j, \Gamma$) collected in Table I are given for the following electronic states of CO: $|o\rangle = X\,^1\Sigma^+$, $|i\rangle = O\,1s^{-1}2\pi^1\,^1\Pi$, $|f\rangle = 1\pi^{-1}2\pi^1\,^1\Delta$ [25]. At this and forthcoming figures the center of gravity is given as a function of a shifted detuning relative to ''vertical'' emission frequency $\widetilde{\epsilon}_{if}^{S}$ (32):

$$\widetilde{\Omega} = \Omega - \Delta,$$

$$\Delta = \left(\frac{\omega_o - \omega_i}{4}\right)\left(1 - \frac{\omega_f^2}{\omega_o\omega_i}\right) + \frac{\mu_f^2}{2}[(R_o - R_f)^2 - (R_i - R_f)^2].$$
$$(35)$$

With this definition for the detuning $\widetilde{\Omega}$ the relative CG $\epsilon(\omega) - \widetilde{\epsilon}_{if}^{S}$ (32) is equal to zero when $\widetilde{\Omega} = 0$ in the Raman limiting case (26). Now the true dispersion line is no longer antisymmetrical relative to the Raman dispersion line (12); compare Figs. 2 and 5.

When the lifetime broadening is small,

$$\Gamma \ll \omega_o, \quad \omega_i, \quad \omega_f \qquad (36)$$

the CG oscillates in the region of photoabsorption but follows closely the Raman law outside of this region (Fig. 5). A comparison of these oscillations with the photoabsorption profile (Fig. 6) shows that the minima of the CG positions correspond approximately to the maxima of the absorption cross section. When the lifetime broadening $\Gamma$ increases, the oscillations of the CG disappear and the deviation from the Raman law (26) also disappears in the limit $\sqrt{\Omega^2 + \Gamma^2} \gg \Gamma_{\text{eff}}$ (Fig. 5). If one ignores the oscillation of CG in the
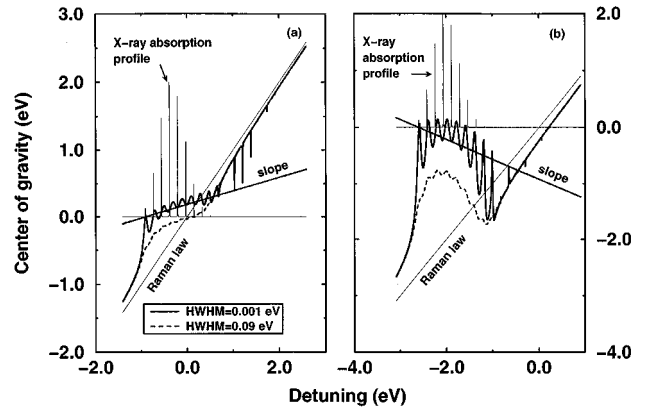
region of photoabsorption one can roughly approximate the behavior of the center of gravity in this region by a straight line,

$$\epsilon(\omega) - \widetilde{\epsilon}_{if}^{S} \simeq \Omega\left(\frac{\omega_i^2 - \omega_f^2}{2\omega_i^2}\right) \qquad (37)$$

but with a slope that is different from the Raman law (26) (we note that this estimation for the slope is good only for a small lifetime broadening).

Figure 6(b) demonstrates the *anti-Raman* behavior of the dispersion law. In this case, contrary to Fig. 6(a) the vibrational frequency of the final state is larger than the one for the core excited state ($\omega_f > \omega_i$) and the slope (37) becomes negative. Numerical investigations show that the slope of Eq. (37) is useful and leads to correct qualitative conclusions only if the function $\rho$ [see Eq. (40)] is positive.

### 1. Asymptotic behavior of CG. Time-dependent approach

Numerical results (Figs. 5 and 6) obtained with help of Eqs. (32) and (34) clearly demonstrate that the frequency dependence of CG is strongly nonlinear and that this dependence qualitatively differs from the three-level model (Fig. 2). Unfortunately, the strict Eqs. (32) and (34) are too complex to obtain simple rules useful for a qualitative analysis of the dispersion. However, one useful parameter was found in Sec. IV C, namely, the slope defined by Eq. (37). The asymptotical behavior of CG gives another useful parameter for the qualitative analysis of the dispersion in the photoabsorption region.

TABLE I. Vibrational frequencies $\omega_j$, equilibrium internuclear distances $R_j$ ($j = o, i, f$), and lifetime broadenings $\Gamma$ for ground ($o$), core-excited ($i$), and final ($f$) states of the CO molecule.

| State | $\omega_j$ (eV) | $R_j$ (Å) | $\Gamma$ (eV) |
|---|---|---|---|
| Ground ($o$):$X\,^1\Sigma^+$ | 0.27 | 1.128 | 0 |
| Core-excited ($i$):O$1s^{-1}2\pi^1\,^1\Pi$ | 0.18 | 1.280 | 0.09 |
| Final ($f$):$1\pi^{-1}2\pi^1|\rangle^1\Delta$ | 0.14 | 1.399 | $\simeq 0$ |

Let us investigate how the exact dispersion law (32) relates to the Raman law (12) when the frequency detuning $\Omega$ is large or when the lifetime broadening $\Gamma$ is large. To accomplish this we start from a time-dependent representation of CG given in the Appendix [Eq. (A6)]. According to the method of stationary phase (A8) the frequency dependence of CG follows very closely the ordinary Raman law (12)

$$\epsilon(\omega) \approx \omega - \epsilon_{fo}^S - \frac{\Omega\omega_i}{\Omega^2 + \Gamma^2}\,\rho, \qquad (38)$$

when the lifetime broadening and/or the detuning frequency is large,

$$\frac{|\Omega|\omega_i}{\Omega^2 + \Gamma^2} \ll 1. \qquad (39)$$

Equation (48) shows directly that in this limit the main contribution to the frequency dependence of CG is given by sudden transitions ($t=0$). The nuclear dynamics influences strongly the asymptotic behavior of CG through the parameter

$$\rho = \frac{\mu\omega_f^2\omega_i}{\omega_o}\,(R_o - R_i)(R_o - R_f) + \frac{(\omega_o^2 - \omega_i^2)(\omega_o^2 - \omega_f^2)}{4\omega_o^2\omega_i}. \qquad (40)$$

This parameter can be positive, negative and equal to zero depending on the precise relation between frequencies and positions of the potential surfaces of the electronic states involved. The asymptot of CG is antisymmetric relative to the Raman-Stokes law (12) if $\rho \neq 0$. When $\rho = 0$ we have to take into account a correction to the Raman law of higher order. One can understand that this correction is proportional to $1/(\Omega^2 + \Gamma^2)$, and, therefore, that the asymptot of CG defines a symmetrical function of detuning for the case $\rho = 0$ [see Fig. 7(b)]. Figure 7 shows that knowledge of the asymptotic behavior allows a prediction of the behaviour of CG in the photoabsorption region using a very simple analysis of the $\rho$ function (40). The change of sign of the $\rho$ function (40) leads to inversion of the CG frequency dependence relative to the Raman dispersion line [compare Figs. 7(a) and 7(b)]. Let us note two special important cases for which $\rho = 0$. This function is equal to zero for example if the potentials of ground and core excited states coincide ($R_o = R_i$, $\omega_o = \omega_i$) or if the potentials of ground and final states coincide ($R_o = R_f$, $\omega_o = \omega_f$). The last case takes place for elastic scattering, as further discussed below.

### 2. Role of interference

Let us now look at the structure of the expression for the CG (32) from the point of view of interference effects. The functions $f_1(\omega)$ and $f_2(\omega)$ [Eqs. (32) and (34)] are caused by lifetime-vibrational interference contributions to the RXS cross section [19,21,26,22], while $f(\omega)$ is the direct term. Figure 8 shows that the lifetime-vibrational interference effect plays a very important role in the dispersion law for the x-ray Raman effect.
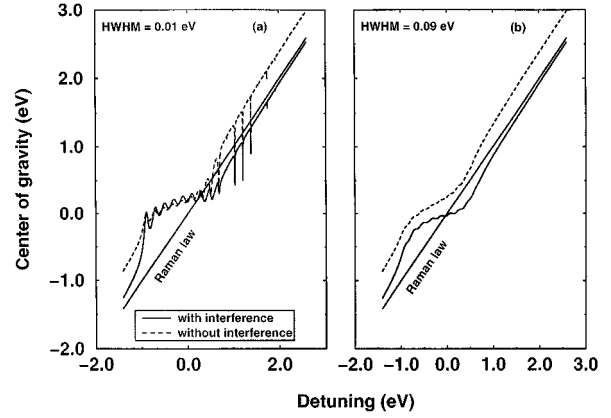


FIG. 7. Influence of nuclear dynamics on the CG spectral shape. Thick solid curves show exact calculations according to Eqs. (32) and (34). Raman law (12) is depicted by dashed lines. Thin solid curves show asymptotical behavior of the center of gravity (38). $\Gamma = 0.09$ eV. (a) $\rho > 0$. Data for O $K$ emission of CO molecule (Table I). (b) $\rho = 0$. Input data are the same as for (a) except data for the final state which coincide with the ground-state data $\omega_f = \omega_o = 0.27$ eV, $R_f = R_o = 1.128$ Å. (c) $\rho < 0$. $\omega_o = \omega_f = 0.27$ eV, $\omega_i = 0.22$ eV, $R_o = 1.128$ Å, $R_i = 1.05$ Å, $R_f = 1.399$ Å.

### 3. Elastic scattering

Until now we considered inelastic x-ray scattering with different initial- and final-state potential surfaces. In the case of elastic RXS these potential surfaces coincide. The dispersion law for elastic RXS is depicted in Figs. 7(b) and 9 using data for the CO molecule. Since here $\omega_o > \omega_i$ this dispersion law shows anti-Raman behavior [see Eq. (37)]. The convergence of the dispersion (32) with respect to the Raman law (12) when the detuning tends to $\infty$ is presented in Figs. 7 and 8. As can be seen in these figures the convergence is slow ($\propto 1/\Omega$) in the general case (Fig. 7) but quite fast ($\propto 1/\Omega^2$) in the case of elastic scattering (Fig. 8).

### V. SUMMARY

We have presented theory for Raman frequency dispersion of x-ray scattering spectra of molecules. Analytical expressions for the frequency dependence of the center of gravity and the width of RXS bands for electron-vibrational transitions have been given and numerically evaluated for different limiting conditions. It has been demonstrated that the RXS dispersion strongly depends on the spectral distribution of the incident light beam and that the RXS dispersion differs qualitatively for broad band and narrow band excitations. In the first case the Raman dispersion of the center of gravity appears only for tail excitation, while for narrow band excitation the dispersion can adopt several characteristic features depending on the precise relation between the parameters of the interatomic surfaces of the electronic states involved.

Our investigations thus show that the RXS dispersion is strongly influenced by nuclear dynamics when the spectral width $\gamma$ of the incident light beam is small. We found that this influence is important in a broad region of incoming photon frequencies $\omega$. When $\omega$ lies outside the absorption band the RXS dispersion follows closely the ordinary Raman law for linear dispersion. The convergence to this Raman
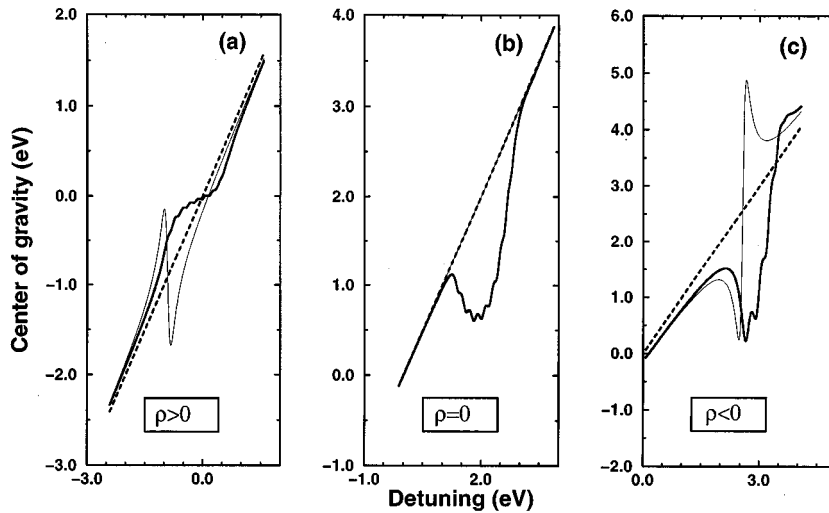
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FIG. 8. Influence of lifetime-vibrational interference on center of gravity. Input data for O $K$ emission of CO molecule (Table I).

law for tail excitation depends, however, strongly on the parameters of the potential surfaces of the states involved in the RXS event. In general, the nuclear dynamics leads to a qualitatively different convergence to the ordinary Raman law in comparison with the atomic case, and if $\omega$ lies within the region of photoabsorption, it totally dictates the spectral shape and the CG. Contrary to the atomic three-level approximation of RXS with an antisymmetrical dispersion law, the vibrational structure leads to an asymmetrical frequency dependence of the CG.

The behavior of the CG in the region of photoabsorption depends strongly on vibrational frequencies and equilibrium geometries of the states involved in RXS. It then shows oscillatory behaviour when the lifetime broadening is small in comparison with vibrational frequencies. These oscillations are quenched when the lifetime broadening increases. The slope of the CG is a striking manifestation of the nontrivial behavior of this quantity. The slope is positive for the ordinary Raman dispersion, but as shown here it can be equal to zero or be negative (*anti-Raman* dispersion), directly correlating with the sign of the difference between vibrational frequencies of the core-excited and final states ($\omega_i - \omega_f$).

There is another parameter except for the slope that governs the dispersion of the CG, namely, the ''potential'' parameter $\rho$ (40), which depends in a simple way on the vibrational frequencies and equilibrium distances of the potentials involved. We found three qualitatively different dispersion dependences of CG that correspond to three different values for this parameter: $\rho<0$, $\rho=0$, and $\rho>0$. The $\rho$ parameter is exactly equal to zero for elastic RXS, while for inelastic RXS it is usually different from zero. The dispersion relations for elastic and inelastic RXS bands are, therefore, qualitatively different.

In addition to the width of the spectral function of exciting radiation, the experimental possibilities to observe the proposed dispersion laws evidently also depend on the resolution of the spectrometer. This resolution is guided by a convolution function that must be tested in each particular experimental situation. At present it seems that the comparatively high intensity of nonradiative RXS gives a better possibility than radiative RXS to reach sufficient resolution in order to test the dispersion effects. In radiative RXS there is also the serious experimental problem of self-absorption for

the elastic band, which may strongly disturb the predicted dispersion law. To observe the true dispersion for an elastic band it will thus be necessary to use an optically thin target.

## ACKNOWLEDGMENT

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## APPENDIX

To calculate the center of gravity we use the following formula for the matrix elements of the operator $V$ (21)

$$
\begin{aligned}
\langle m_1|V|m\rangle = & \left(\frac{\mu}{2\omega_i}\right)^{1/2} \omega_f^2 (R_i - R_f) [\sqrt{m}\,\delta_{m_1,m-1} \\
& + \sqrt{m+1}\,\delta_{m_1,m+1}] + \frac{\omega_f^2 - \omega_i^2}{4\omega_i}\,[(2m+1)\delta_{m_1,m} \\
& + \sqrt{m(m-1)}\,\delta_{m_1,m-2} \\
& + \sqrt{(m+2)(m+1)}\,\delta_{m_1,m+2}]
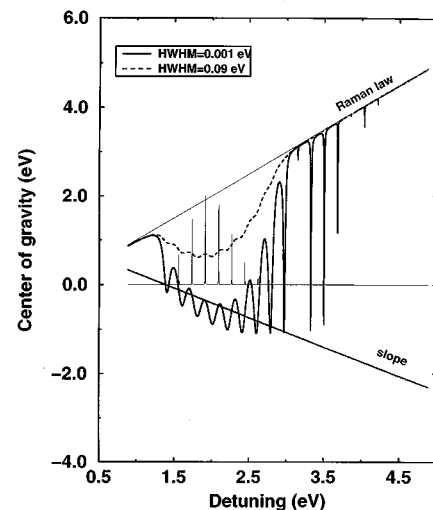\end{aligned}
\tag{A1}
$$



FIG. 9. Influence of nuclear dynamics on the center of gravity of elastic RXS. Data for O $K$ emission of CO molecule (Table I). Potential surfaces of initial ground and final states coincide.

and the expression for the Franck-Condon (FC) factors $\langle m|o\rangle$ between the ground-state vibrational wave function $|o\rangle$ and the vibrational wave function $|m\rangle$ of the core excited intermediate state $i$ of the diatomic molecule. This FC factor is expressed in the harmonic approximation through the Hermite polynomial $H_m(z)$:

$$\langle m|o\rangle = \zeta\,\frac{q^{m/2}}{\sqrt{m!}}\,H_m(z). \tag{A2}$$

The parameters defining the FC factor

$$\zeta = \frac{(4\omega_o\omega_i)^{1/4}}{(\omega_o+\omega_i)^{1/2}}\exp\left(-\frac{\mu\omega_o\omega_i}{\omega_o+\omega_i}(R_o-R_i)^2\right),$$

$$q = \frac{1}{2}\frac{\omega_o-\omega_i}{\omega_o+\omega_i}, \quad z = (R_o-R_i)\left(\frac{\mu\omega_i}{[1-(\omega_i/\omega_o)^2]}\right)^{1/2}, \tag{A3}$$

depend on the vibrational frequencies $(\omega_o,\omega_i)$ and the equilibrium internuclear distances $(R_o,R_i)$ of ground $o$ and core excited $i$ states.

To evaluate the asymptotic behavior of the CG the following summations are needed:

$$\sum_{m=0}^{\infty} m|\langle m|o\rangle|^2 = \frac{1}{2}\left(\mu\omega_i(R_o-R_i)^2+\frac{(\omega_o-\omega_i)^2}{2\omega_o\omega_i}\right),$$

$$\sum_{m=0}^{\infty}\sqrt{(m+1)(m+2)}\langle o|m\rangle\langle m+2|o\rangle$$

$$= \frac{1}{2}\left(\mu\omega_i(R_o-R_i)^2-\frac{(\omega_o-\omega_i)^2}{2\omega_o\omega_i}\right), \tag{A4}$$

$$\sum_{m=0}^{\infty}\sqrt{(m+1)}\langle o|m\rangle\langle m+1|o\rangle = (R_o-R_i)\sqrt{\frac{\mu\omega_i}{2}}.$$

These expressions are obtained in accordance with the following equation [27]:

$$\sum_{k=0}^{\infty}\frac{t^k}{k!}H_{k+m}(x)H_{k+n}(x)$$

$$= (1-4t^2)^{-(m+n+1)/2}\exp\left(\frac{4tx}{1+2t}\right)\times\sum_{k=o}^{\min(m,n)}2^{2k}k!\binom{m}{k}$$

$$\times\binom{n}{k}t^k H_{m-k}\left\{x\left(\frac{1-2t}{1+2t}\right)^{1/2}H_{n-k}\left[x\left(\frac{1-2t}{1+2t}\right)^{1/2}\right]\right\}. \tag{A5}$$

### Time-dependent representation of the center of gravity

Here we give some equations which are necessary for the evaluation of the asymptote of the center of gravity for large detuning (39). For this purpose it is more natural to use a time-dependent representation of CG. From the time-dependent representation for the absorption cross section $\sigma_o(\omega)$ (30) and the functions $f(\omega)$, $f_1(\omega)$, $f_2(\omega)$ (34) one can receive with a help of Eq. (A5),

$$\sigma_o(\omega) = \frac{1}{\Gamma}\,\mathrm{Re}\int_0^\infty dt\,e^{i(\Omega+i\Gamma)t}\chi(\tau),$$

$$f(\omega) = \frac{4}{\Gamma}\,\mathrm{Re}\int_0^\infty dt\,e^{i(\Omega+i\Gamma)t}\chi(t)\frac{\tau\chi(t)}{1-4\tau^2}\left[z^2\left(\frac{1-2\tau}{1+2\tau}\right)+1\right], \tag{A6}$$

$$f_1(\omega) = 2z\sqrt{q}\,\mathrm{Im}\,\frac{1}{\omega_i-i\Gamma}\int_0^\infty dt$$

$$\times\left[e^{i(\Omega-\omega_i+i\Gamma)t}\frac{\chi(t)}{1+2\tau}+e^{-i(\Omega-i2\Gamma)t}\frac{\chi^*(t)}{1+2\tau^*}\right],$$

$$f_2(\omega) = q\,\mathrm{Im}\,\frac{1}{\omega_i-i\Gamma}\int_0^\infty dt$$

$$\times\left\{e^{i(\Omega-2\omega_i+i\Gamma)t}\frac{\chi(t)}{1-4\tau^2}\left[2z^2\left(\frac{1-2\tau}{1+2\tau}\right)+1\right]\right.$$

$$\left.+e^{-i(\Omega-i\Gamma)t}\frac{\chi^*(t)}{1-4\tau^{*2}}\left[z^2\left(\frac{1-2\tau^*}{1+2\tau^*}\right)+1\right]\right\},$$

where

$$\tau = qe^{-i\omega_i t}, \quad \chi(t) = \frac{\zeta^2}{\sqrt{1-4\tau^2}}\exp\left(\frac{4\tau z}{1+2\tau}\right). \tag{A7}$$

The high-frequency asymptote for the center of gravity (32) can be received by a direct, but somewhat lengthy, evaluation of Eqs. (A6) using the method of stationary phase,

$$\int_0^\infty e^{i(\Omega+i\Gamma)t}\phi(t)dt\approx\frac{i\phi(0)}{\Omega+i\Gamma}-\frac{\phi'(0)}{(\Omega+i\Gamma)^2} \tag{A8}$$

applied to the limiting case (39).

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