multipoles leads to additional sums for every included multipole polarizability. Their inclusion is important, because it was observed[5,20] that the contribution of the third-order dipole-dipole-quadrupole term to the cohesion energy of noble gases largely cancels the fourth-order pure-dipole contribution. Inclusion of hyperpolarizabilities leads to connected rings. The fact that the result is analytic should allow its use for the calculation of liquid and solid properties.

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Theory of Induced Molecular-Orbital *K* X Rays in Heavy-Ion Collisions*

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The mechanisms of spontaneous and induced emission of radiation are derived from the Dirac equation in a rotating coordinate system. The molecular-orbital x-ray spectra exhibit a strong asymmetry with respect to the beam axis. The asymmetry peaks for the high-energy transitions, which can be used for spectroscopy of two-center orbitals.

During collisions of heavy ions with heavy targets at moderate energies (below the Coulomb barrier) intermediate molecular electronic states will be formed. It has been expected that the direct proof for this theoretical prediction would consist in the observation of radiative transitions between such molecular states.[1] Indeed, reports on the detection of molecular x rays have been given by various experimental groups.[2] However, background effects such as electronic and nuclear bremsstrahlung occur as competing effects in these measurements. Only recently Greenberg, Davis, and Vincent[3] have carried out experiments with monoisotopic Ni beam and target where nuclear dipole bremsstrahlung is forbidden.

The unique signature of molecular x rays comes from the fact that—contrary to atomic x rays—in addition to the *spontaneous* x rays *induced* radiative transitions also occur, which can be recognized by their asymmetric angular distribution relative to the beam axis. It is the purpose of this note to discuss the x-ray spectrum due to

both spontaneous and induced transitions including the most important dynamical effects.

The adiabatic molecular states are given by the two-center Dirac equation given by Müller, Rafelski, and Greiner.[4] Nonadiabatic effects and radiative coupling can be described by writing the generally covariant form of the Dirac equation[5,6] in a rotating, instantaneous, coordinate system whose z axis is along the line connecting the two scattering nuclei[6]:

$$\gamma^k\left(\frac{\partial}{\partial x^k}-\frac{ie}{\hbar c}A_k+\Gamma_k\right)\Psi+\frac{m_e c}{\hbar}\Psi=0. \tag{1}$$

The $\Gamma_k=\frac{1}{4}\gamma^i(\gamma_{i|k}-\{{}^{e}_{ix}\}\gamma_e)-\frac{1}{32}\mathrm{Tr}(\gamma\gamma^i\gamma_{i|k})\gamma$ are the generalized connections for spinor differentiation, and the Dirac matrices γ^k are determined via the metric g^{ik} of the coordinates in the rotating frame.[6] Explicit evaluation for a system with angular velocity $\vec{\omega}_{\mathrm{rot}}(t)$ gives

$$i\hbar\,\partial\psi/\partial t=\{c\vec{\alpha}\cdot[\vec{p}-(e/c)\vec{A}]+V+\beta m_e c^2\}\psi-\vec{\omega}_{\mathrm{rot}}\cdot\{\vec{r}\times[\vec{p}-(e/c)\vec{A}]+\tfrac{1}{2}\hbar\sigma\}\psi-(i\hbar/4c)(\dot{\vec{\omega}}_{\mathrm{rot}}\times\vec{r})\cdot\vec{\alpha}\psi. \tag{2}$$

Two mechanisms for photon emission are a spontaneous one via the operator $H_{\mathrm{rad\,spon}}=e\vec{\alpha}\cdot\vec{A}=-i(e/\hbar)\times[H,\vec{r}]\cdot\vec{A}$ and an induced emission caused by $H_{\mathrm{rad\,ind}}=(e/c)\vec{\omega}_{\mathrm{rot}}\times\vec{r}\cdot\vec{A}$, where the former current is imaginary while the latter is real. Therefore no interference occurs and the cross section for the two processes is given in the approximation of Fermi's Golden Rule by[6,7]

$$\frac{d\sigma_{\mathrm{spon}}}{d\omega\,d\Omega_K\,d\Omega_{\mathrm{ion}}}=\frac{\omega^2}{2\pi\hbar c^3}|d_{fi}|^2\sin^2\theta_{kd}\left(\frac{d\sigma}{d\Omega_{\mathrm{ion}}}\right)_{\mathrm{Ruth}},\quad \frac{d\sigma_{\mathrm{ind}}}{d\omega\,d\Omega_K\,d\Omega_{\mathrm{ion}}}=\frac{\omega\omega_{\mathrm{rot}}{}^2}{2\pi\hbar c^3}\left|\frac{\vec{I}}{|I|}\times\vec{d}_{fi}\right|^2\sin^2\theta\left(\frac{d\sigma}{d\Omega_{\mathrm{ion}}}\right)_{\mathrm{Ruth}}. \tag{3}$$

Averaging over all possible orientations of the molecular dipole $\vec{d}_{fi}$ (closed shells!) gives a uniform distribution for the spontaneous radiation, and for the induced radiation a distribution

$$d\sigma_{\mathrm{ind}}/d\omega\,d\Omega_K\,d\Omega_{\mathrm{ion}}\propto 1-\tfrac{1}{2}\sin\theta_{KI},$$

where θ_{KI} is the angle between the photon and the rotation axis $\vec{I}/I$, or if we integrate also over the azimuthal ion scattering angle

$$d\sigma_{\mathrm{ind}}/d\omega\,d\Omega_K\sin\theta_{\mathrm{ion}}\,d\theta_{\mathrm{ion}}\propto\tfrac{1}{2}+\tfrac{1}{4}\sin^2\theta_K,$$

where θ_K is the angle between the photon and the beam axis. Only the $2p_{3/2}\sigma$, $2p_{3/2}\pi$, and $2p_{1/2}\sigma$ to $1s_{1/2}\sigma$ transitions are included in our calculations. They are so far assumed to be equally occupied with electrons. Unequal population (alignment) of the $2p_{3/2}\pi$, $2p_{3/2}\sigma$, and $2p_{1/2}\sigma$ molecular orbitals (MO's) with probabilities A^2, B^2, and C^2, respectively, leads to the following asymmetry as a function of photon energy $\hbar\omega$, photon scattering angle θ_K, and ion energy E:

$$\eta(\omega,\theta_K,E)=\frac{d\sigma(\theta_K)}{d\omega\,d\Omega_K}\left(\frac{d\sigma(\theta_K=0)}{d\omega\,d\Omega_K}\right)^{-1}-1=\frac{3}{2}\sin^2\theta_K\frac{A^2-B^2-(A^2-\frac{7}{3}B^2-\gamma C^2)\alpha_3{}^2}{3A^2+5B^2+6\beta C^2+(3A^2+B^2+3\gamma C^2)\alpha_3{}^2}, \tag{4}$$

where $\beta=D_1{}^2/D_3{}^2$ is the ratio of the square of the induced dipole matrix elements of the $2p_{1/2}\sigma$ and $2p_{3/2}\pi,\sigma$ to the $1s_{1/2}\sigma$ states, $\gamma=D_1{}^2\alpha_1{}^2/D_3{}^2\alpha_3{}^2$, and $\alpha_v=v/R_v(\omega)\omega=(2ME)^{1/2}/R_v(\omega)\omega$. $R(\omega)=R_0[(\omega_c-\omega)/(\omega-\omega_s)]^{1/2}$ is the (approximate) two-center distance as a function of the photon energy. For the $2p_{1/2}$ MO one has $\hbar\omega_s=0$ and $\hbar\omega_c=31.8$ keV, and for the $2p_{3/2}$ MO, $\hbar\omega_s=7.5$ keV and $\hbar\omega_c=34$ keV. $R_0=2100$ fm. Obviously η is largest perpendicular to the beam axis ($\theta_K=90°$). The comparison of (4) with experiments[3] can serve as a determination of the alignments A^2/B^2 and A^2/C^2.

As a result of the nonadiabatic effects the molecular states obtain a width $\Gamma(t)$ which is composed of three different parts[7]:

$$\Gamma_{\mathrm{rad\,spon}}=\sum_{nk\epsilon}|e(2\pi/\hbar\omega)^{1/2}\int_0^t dt'\exp[i\int_0^{t'}d\tau\,\omega_{mn}(\tau)+i\omega t']\,\omega_{mn}\langle n(R)|\vec{r}\circ\vec{A}|m(R)\rangle|^2,$$

$$\Gamma_{\mathrm{rad\,ind}}=\sum_{nk\epsilon}|e(2\pi/\hbar\omega)^{1/2}\int_0^t dt'\exp[i\int_0^{t'}d\tau\,\omega_{mn}(\tau)+i\omega t']\,\vec{\omega}_{\mathrm{rot}}\times\langle n(R)|\vec{r}\circ\vec{A}|m(R)\rangle|^2, \tag{5}$$

$$\Gamma_{\mathrm{non\,rad}}=\sum_{n\neq m}|\int_0^t dt'\exp[i\int_0^{t'}d\tau\,\omega_{mn}(\tau)]\langle n(R)|\dot{R}\,\partial/\partial R+\vec{\omega}_{\mathrm{rot}}\cdot\vec{J}/\hbar|m(R)\rangle|^2,$$

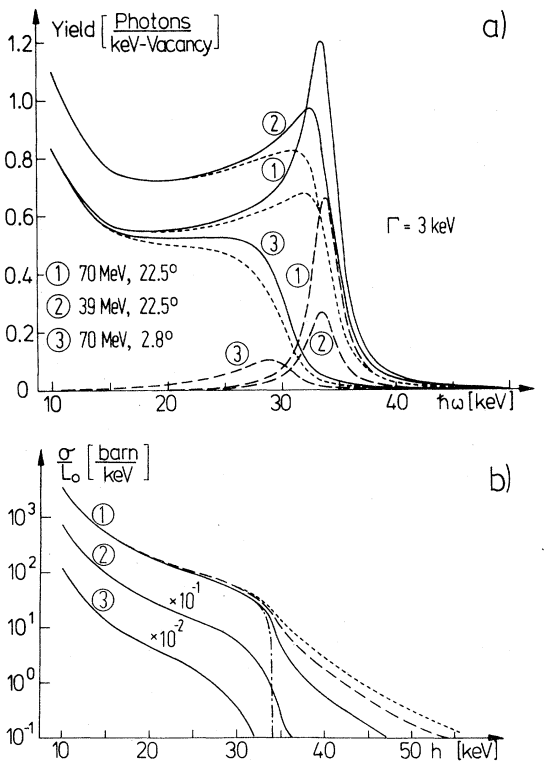

FIG. 1. (a) The MO x-ray yield for coincidence experiments with 70-MeV Ni-Ni at (1) 11.2° and (3) 1.4° scattering angle, and (2) 39-MeV Ni-Ni at 11.2° scattering angle (all quantities in the lab system). The solid lines show the total yield; the dotted and dashed lines the spontaneous and induced contributions, respectively. Observe that the peaks are strongly enhanced by the induced-emission mechanism. (b) MO x-ray cross sections for the singles experiment Ni-Ni. (1) Yield for 70-MeV collision. The solid line corresponds to $\Gamma = 1$ keV, the dashed and dotted lines to 3 and 5 keV, respectively. The dashed-dotted lines give the spectrum without collision broadening which sharply cuts off at the limiting atom $K\alpha$ energy. (2) Spectrum for 19-MeV collision, (3) for 5 MeV, both with $\Gamma = 1$ keV. All quantities in the lab system.

where S represents integration or summation as appropriate. In our present calculations an effective parameter Γ has been chosen for the sum of these widths,[7] and has been varied between 1 and 5 keV to establish the dependence of the spectra on the width which is a function of scattering energy ($\Gamma \sim \sqrt{E}$). It leads to a smooth transition from the molecular x-ray spectrum into the quadrupole bremsstrahlung background,[8] which can serve for its determination [see Fig. 1(b) above]. Moreover, we have neglected interference effects of the radiation for high-energy x-ray transitions.[9] The cross sections are calculated here by integrating (3) along the trajectory and, for the singles spectrum, by further integrating over all ion scattering angles. The transition energies and dipole matrix elements are taken from the exact relativistic one-electron states for the Ni-Ni system.[4,10] For the symmetric Ni-Ni collision, the symmetrized Rutherford cross section is used. The results for a coincidence experiment (equal population assumed) at various scattering angles and energies are shown in Fig. 1(a). The spectra at moderate forward angles exhibit a pronounced peak at the high-energy end which is essentially due to the additional induced radiation that is strongly peaked at high photon energies. The induced radiation also grows with increasing scattering energy, whereas the spontaneous yield per K vacancy drops. Of course, the K-vacancy production will increase with rising energy. For low scattering energy (e.g., 5 MeV) the molecule no longer reaches the asymptotic "runway" region[4] and no peak structure occurs. For very forward or more backward angles ($\theta < 10°$, $\theta > 45°$) the contribution from induced radiation decreases with respect to the spontaneous x-ray yield. Especially for very forward angles ($\theta < 3°$) the runway region is forbidden and the peak vanishes altogether [Fig. 1(a)]. The width of the peak at the end of the spectra at forward angles is almost completely determined by the collision broadening $\Gamma(t)$ and not so much by the shape of the level diagram. For the singles experiment the spectra shapes look essentially exponential [Fig. 1(b)]. The calculation assumes that a K vacancy is brought into the collision (two-step process). For a one-step process (ionization and x ray in the same collision) the impact-parameter dependence of K-vacancy production has to be folded into the integration over Rutherford cross section. The end point of the spectrum is a function of scattering energy, because Γ itself increases with scattering energy. For very low scattering energies, e.g., 5 MeV in Fig. 1(b), the experimental end point of the spectrum may even lie before the united-atom limit as the asymptotic region of the level diagram is not reached in the collision. For comparing theory with experiment we note that the backgrounds of the tails of the atomic $K\alpha, \beta$ lines, the electron bremsstrahlung, transitions from higher MO's, and also the contribution of the slower recoil ions to the MO x-ray production[3] are expected to contribute mostly in the low-energy part of the x-ray continuum. This leads to a greater "filling up" of the spectrum shown in

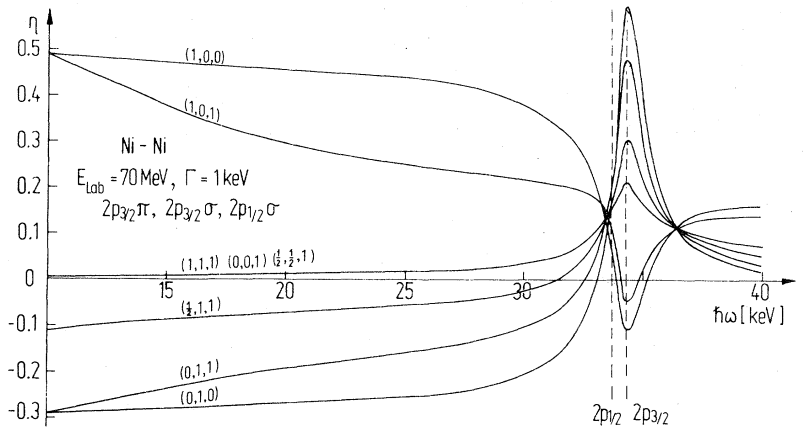

FIG. 2. The asymmetry as a function of photon energy for 70 MeV Ni-Ni collisions. The alignment (A^2, B^2, C^2) is indicated.

Fig. 1(b) at lower energies. It will be discussed in a forthcoming paper. The asymmetries (4) are shown in Fig. 2 for various alignments. For not too small scattering energies they show a practically linear dependence on energy, which is to a large extent compensated by the inverse energy dependence of the width Γ. They exhibit a strong dependence on photon energy $\hbar\omega$, which is entirely due to the induced transitions. The observation of this effect by Greenberg, Davis, and Vincent[3] uniquely proves the existence of molecular x rays and of induced transitions at the same time.

The shape (peaking) of the coincidence spectra gives great hope for future spectroscopy of two-center orbitals. In Ni-Ni collisions, e.g., it should ultimately be possible to determine the center of the peak to within a few hundred eV. This general feature should also hold for much heavier systems because the induced radiation always comes from the "compound-atom" region of the two-center level diagram. Experimentally this opens up the completely new field of x-ray spectroscopy of superheavy molecules which is of fundamental interest for quantum electrodynamics of strong fields. For example, in a system with $Z_1+Z_2 \sim 150$ the contribution of vacuum polarization from the Uehling potential is expected to be of the order of 5 keV for the $2p_{3/2}$-$1s_{1/2}$ transition and exceeds the self-energy contribution. Thus it would be for the first time possible to measure vacuum polarization as the dominant quantum electrodynamical effect.

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[9]Note that the expressions (5) and similar ones for the cross section show "rainbow effects" due to the time dependence of the matrix elements, of $\omega_{mn}(t)$, and of $\Gamma(t)$ itself. These effects shall be separately

investigated in a forthcoming paper. Since these interference effects show up where the phase difference between contributions from approaching and leaving ions along the scattering trajectory are largest, they should occur most pronounced for low-energy transitions and their oscillation frequency should increase with bombarding energy of the ions.

[10]We acknowledge help in the calculations by W. Betz.

Evidence for Quasimolecular K X-Ray Emission in Heavy-Ion Collisions from the Observation of the X-Ray Directional Anisotropy*

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We have observed an anisotropic angular distribution for the high-energy continuum x rays emitted in high-energy collisions of Ni ions with Ni atoms. The variation of the anisotropy with photon energy is uniquely characteristic of induced radiative transitions in quasimolecules, and hence provides strong evidence for the quasimolecular origin of these radiations.

A search for the formation of intermediate electronic molecules in close collisions of very heavy ions has been motivated recently by the prospect that such united atom phenomena may ultimately provide access to the spectroscopy of superheavy atoms and, therefore, to fundamental processes associated with the quantum electrodynamics of strong fields.[1] Proof for the existence of such quasimolecules has been sought in the emission of K x-ray radiation from transitions between the molecular orbitals that may be formed in the collision.[2-6] In this paper we report on the results of an investigation to detect such transitions in the ^{58}Ni+^{58}Ni ion-atom system colliding at high energy. We discuss particularly the observation, for the first time, of a directional asymmetry for the high-energy continuum x rays emitted in the collision, which we utilize as a distinctive characteristic for identifying the quasimolecular origin of these radiations.

Studies with light-ion-atom systems have provided some of the more convincing demonstrations of molecular orbital x-ray emission.[2,5] However, the interpretation of experiments involving high-energy collisions of heavy-ion-atom systems,[3,4] which are more relevant to the future investigations noted above, are presently more speculative, relying on an ability to extrapolate detailed identifying features from mechanisms found applicable previously in light systems. The interpretation of these experiments is particularly complicated by the exponential energy dependence of the continuous spectra observed, by uncertainties with regard to the mechanisms dominating K-vacancy production during high-energy heavy-ion collisions, by collision broadening effects, and most important, by the lack of a definitive signature for distinguishing this radiative process from other competing radiations.[4]

Recently, Müller, Smith, and Greiner[7] have noted that the characteristic angular distribution expected for molecular orbital K x-ray emission furnishes such a unique signature. This suggestion centers on the existence of the important, but previously neglected, induced transitions between molecular orbitals which specifically reflect the nonstationary character of the molecular electronic states as they adjust to the rotation of the internuclear axis. Reflecting the nuclear motion, the induced transitions can only be associated with the formation of quasimolecules. They add incoherently to the spontaneous molecular transitions with a relative intensity that grows with increasing photon energy. In the absence of a spatial alignment of the molecular orbitals, the induced radiations are predicted to exhibit an angular emission pattern relative to the ion-beam axis of the form $\frac{1}{2}+\frac{1}{4}\sin^2\theta$, while the spontaneous radiations are expected to be isotropic.[7] Thus the incoherent sum of the two produces a prominent enhancement of the angular distribution asymmetry near the united atom K x-ray energy.[8] As demonstrated in Ref. 8 we note that although an alignment of the molecular orbitals may modify these features quantitatively by changing the angular distributions of both the induced and spontaneous transitions, the observation of an anisotropy which peaks near the