Radiative Transitions between Quasimolecular Levels During Energetic Atom-Atom Collisions

F. W. Saris, W. F. van der Weg,* and H. Tawara†
Foundation for Fundamental Research on Matter, Institute for Atomic and Molecular Physics, Kruislaan 407, Amsterdam, The Netherlands

and

Roman Laubert‡
Department of Physics, New York University, New York, New York 10003
(Received 1 February 1972)

We report the observation of an x-ray band which cannot be identified as a characteristic atomic x ray either of the target atoms or of the projectiles. The new x ray has been observed when 70–600-keV argon ions impinge on C, Al, Si, and Fe targets. We attribute this x ray to a radiative filling of a vacancy in the $2p\pi$ orbital of the Ar-Ar system during the collision.

Electrons from atomic shells are excited when electron clouds interpenetrate in energetic atom-atom collisions.[1] The exchange forces generated by the Pauli exclusion principle operating in the interpenetrating electron clouds of the colliding atoms is the dominant mechanism of excitation.[2] Some experimental investigations[1] of these encounters show discrete steps in the inelastic energy-loss spectrum at various internuclear distances. Copious x rays as well as showers of electrons are observed which have been attributed to radiative or Auger transitions following inner-shell ionization of the colliding atoms. To date, all of the observed x rays have been identified as characteristic atomic x rays of the collision partners.

In this paper we report the observation of a broad x-ray line, or an x-ray band, that cannot be identified as a characteristic x ray either of the target atoms or of the projectiles. Specifically, this x-ray band has been observed when 70–600-keV argon ions impinge on C, Al, Si, and Fe targets. From the experimental results we deduce that these x rays originate from Ar-Ar collisions inside the target. We find the production cross section to be increasing with the atomic density of the target. From this we conclude that the projectile must make at least two atomic collisions to produce these x rays: The first, with a target atom, creates an L-shell vacancy in the moving argon ion, and the second, with an argon atom implanted in the target, leads to a radiative decay of this vacancy *during* the collision. We are led to this assignment by considering transient molecular levels of argon atoms in collision.[3] This permits us to attribute the x-ray band to the radiative filling of a vacancy in the $2p\pi$ level of the Ar-Ar system during the collision.

The experimental arrangement is described in detail elsewhere.[4,5] A mass- and energy-analyzed $^{18}Ar_{40}$ ion beam in the energy range 70–600 keV impinges on high-purity targets of C, Al, Si, or Fe. The emitted x rays are registered and energy analyzed by a Si(Li) x-ray detector with a resolution, as measured by the full width at half-maximum (FWHM), of 0.23 keV for 6.4-keV x rays. Typical spectra recorded for thick silicon (metal purity 99.999 999 9%) and carbon (metal purity 99.999%) targets are shown in Fig. 1.

We observe that, for example, ~100-keV argon ions produce a broad x-ray line with a cen-

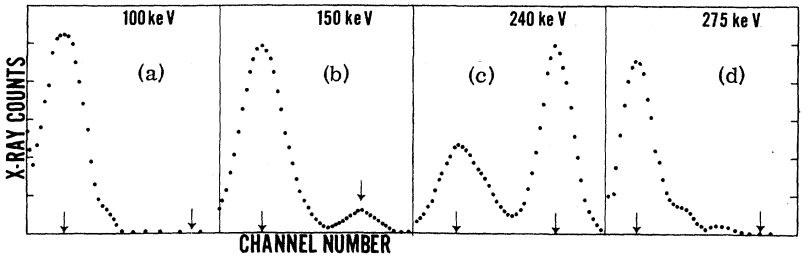

FIG. 1. Typical recorded spectra when argon ions are incident on silicon, (a)–(c), and carbon, (d), targets. The first arrow marks the channel number corresponding to the centroid of a 1.0-keV x ray. The second arrow marks the Si(K) x ray (1.74 keV) in (a)–(c) and the Ar(K) x ray (2.96 keV) in (d).

troid at a channel position which corresponds to a 1.0-keV x ray [Fig. 1(a)]. This broad x-ray line, or x-ray band, is distinctly separated from and bracketed by the characteristic x-ray lines of Ar(L) (0.22 keV) and Si(K) (1.74 keV). On increasing the beam energy the centroid of the x-ray band shifts from ~0.95 keV at 70-keV to ~1.05 keV at 240-keV incident energy [Fig. 1(c)]. The width of the x-ray line, as measured by the FWHM, is 40% to 100% wider than it would be for characteristic target x rays. A broad x-ray line very similar in energy and intensity to the x-ray band observed in Si is detected in all of the other targets. In the case of a carbon target there is no characteristic target x ray on the high-energy side of the x-ray band, and we find that the energy of the emitted x rays is extended considerably [Fig. 1(d)].

In Figs. 1(b) and 1(c) an additional x-ray line is observed which is identified as the Si(K) x ray. The intensity of the Si(K) line increases rapidly with beam energy so that above 300 keV the x-ray band can barely be resolved from the Si(K) line. The Ar(K) x-ray line (2.96 keV) appears with low intensities at energies $\gtrsim$ 300 keV. We find the centroids and width of the Si(K) and Ar(K) x-ray lines to be the same as those observed with protons and Si or Ar targets.

One should not seek the origin of the x-ray band in target impurities or in ion-target interactions alone, since the band occurs for all targets investigated. This leads one to the conclusion that these x rays are due to an Ar-Ar interaction. It follows then, that the intensity must increase with dose, since some of the argon atoms are retained in the target. Indeed, this is observed experimentally. For example, for 200-keV Ar – Si the intensity of the x-ray band increases by a factor of 4 over that observed in the first run (for a dose of ~10^{15} atoms/cm^2), and reaches a saturation value at doses in excess of ~10^{17} atoms/cm^2. Meanwhile, the Si(K) x-ray intensity remains constant.

In search for the origin of these new x rays we view the colliding atoms as a diatomic molecule with varying internuclear distances. For the Ar-Ar system, Lichten[3] has constructed the energy-level diagram of diabatic molecular orbitals shown in Fig. 2. At large internuclear distances the energy levels are those of Ar, while at zero internuclear distance they are those of the united atom Kr. At intermediate distances, electrons form molecular orbitals in compliance with the Pauli exclusion principle operating between the

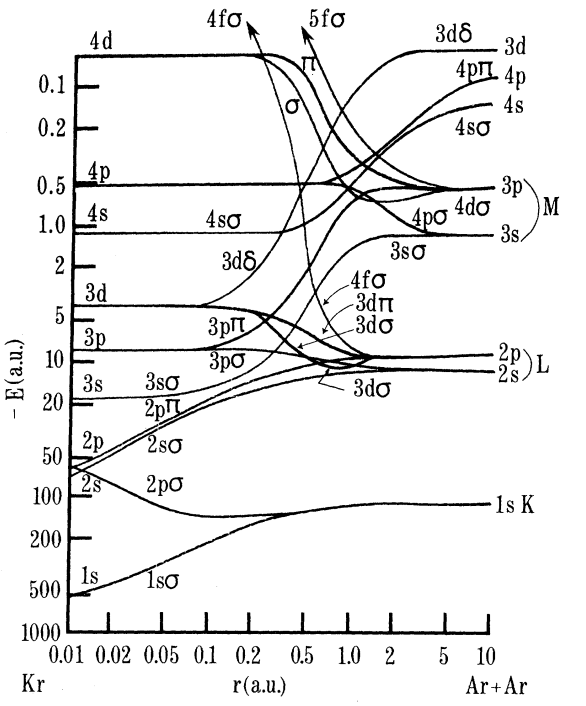

FIG. 2. Energy levels of molecular orbitals for the Ar-Ar system (Ref. 5).

occupied atomic states.

In this scheme the x-ray band, centered near 1 keV, can be attributed to the radiative filling of a previously formed vacancy carried into the $2p\pi$ molecular orbital during an Ar-Ar encounter. For this process to occur we require that the Ar projectile has a $2p$ vacancy prior to such an Ar-Ar collision. During the collision this Ar $2p$ vacancy may follow the $2p\pi$ orbital as the internuclear distance shrinks and ends up as a $2p$ vacancy in the electronic configuration of the "combined" atom, which approaches that of a krypton atom. For the filling of this vacancy to occur *during* the collision, the lifetime of the vacancy must be of the same order as the collision time, which is ~10^{-16} sec for argon ions of keV energy. It is known that the lifetime of a $2p$ vacancy in Kr is 1 order of magnitude shorter than the lifetime of a $2p$ vacancy in Ar, viz., ~4×10^{-16} sec versus ~4×10^{-15} sec.[6,7] Consequently, in close Ar-Ar encounters the lifetime of a vacancy in the $2p\pi$ orbital could in fact be comparable to the collision time. In addition, the observation of this transition should be aided by the fact that the fluorescence yield of the Kr L shell is some 100 times larger than that of the Ar L shell.[7]

From inspection of Fig. 2, we note that the en-

ergy difference between the $3d$ and $2p$ orbitals varies with internuclear distance, from a few hundred electron volts up to 1.6 keV. Thus, in contrast to sharp characteristic x-ray lines of isolated atoms, the x rays emitted by the combined atoms during the collision [molecular orbital (MO) x rays] are expected to have a distribution of energies which shift to higher values as the collision energy increases. The observed x-ray band shows precisely this type of behavior (Fig. 1). In this respect it should be noted that the energy of the characteristic x rays excited by atoms are generally found to be slightly higher ($\lesssim 5\%$) than x rays obtained by proton or electron excitation.[8] This increase in the characteristic x-ray energy is indicative of changes in the external screening during the de-excitation process,[8] which can be attributed to multiple vacancy formation during the collision or to vacancy formation in the aftermath of the collision-induced atomic excitations.[9] At the impact energies we consider here, the changes in screening are not sufficient to account for the observation of the x-ray band nor for the observed widths or energy shifts of the x-ray band.

An x-ray band corresponding to a combined atom of Ar–target-atom encounters is not observed with intensities approaching the intensity of the x-ray band attributed to Ar-Ar encounters. This is surprising, since the target-atom density is at least 1 order of magnitude greater than that of the implanted Ar. Still, x-ray distributions are observed [Fig. 1(d)] which differ from the Ar-Ar x-ray band. However, the small intensities of these distributions, relative to the Ar-Ar x-ray band and characteristic atomic x-ray intensities, prohibit any meaningful analysis at the present time.

One of the essential requirements for the emission of the "MO x rays" is that a $2p$ vacancy in the Ar projectile be brought to the Ar-Ar encounter. Most solid targets can create such conditions because in the penetration process Ar L-shell vacancies are created copiously and because argon atoms become implanted with sufficient concentrations to make Ar-Ar encounters likely before the decay of a previously created Ar L-shell vacancy. From measured values of the Ar L-shell ionization cross section[10] we estimate that as much as 10% of the argon beam in the target will carry the required L-shell vacancy.

The requirements for observing the x ray of the combined atoms (MO x ray) are rather stringent and can be summarized as follows: The time between collisions has to be less than the lifetime of the projectile inner-shell vacancy, and the collision time has to be the order of the lifetime of the vacancy in the combined atom. Nevertheless, it would appear that these requirements can be met in many systems, and experimental observation of the combined atom x-ray line should be feasible in symmetric as well as asymmetric projectile-target systems.

If the mean time between collisions is of importance for the observation of the x-ray band, then its x-ray production cross section must depend on the atomic density of the target. This is amenable to experimental verification. By using a standard procedure,[4] the production cross section is determined to be $\sim 10^{22}$ cm^2 for 250-keV Ar ions incident on Ar-saturated Si targets. In a similar experiment with a dilute Ar-gas target, where the time between collisions was about 8 orders of magnitude longer than in the solid target, we were unable to detect x rays other than Ar(L). This allows us to estimate an *upper* limit to the above cross section in an Ar-gas target to be less than $\sim 10^{-25}$ cm^2. These experimental results are consistent with the requirement that the time between collisions has to be less or on the order of the lifetime of the projectile inner-shell vacancy.

It appears that the molecular orbital scheme of atomic collisions[3] requires that colliding atoms bring a vacancy into a collision to produce even the observed characteristic x-ray lines of Si(K) and Ar(K) (Fig. 1), as well as for many other heavy-projectile–target combinations. This inference should lend itself to experimental scrutiny by experiments similar to the one described here, where the time between collisions is changed in a systematic manner relative to the vacancy lifetimes.

---

*Permanent address: Philips Research Laboratory, Amsterdam, The Netherlands.

†On leave of absence from Nuclear Engineering Department, Kyushu University, Fukuoka, Japan.

‡Work supported by the U. S. Atomic Energy Commission and the New York University Arts and Science Research Fund.

[1]For a recent review of this field, see *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, 1971,* edited by T. R. Govers and F. J. de Heer (North-Holland, Amsterdam, 1971).

[2]W. Brandt and R. Laubert, Phys. Rev. Lett. 24, 1037

(1970).
[3]W. Lichten, Phys. Rev. 164, 131 (1967).
[4]W. Brandt, R. Laubert, and I. Sellin, Phys. Rev. 151, 56 (1966).
[5]W. F. van der Weg, to be published.
[6]D. L. Walters and C. P. Bhalla, in *Seventh International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers*, edited by L. M. Branscomb *et al.* (North-Holland, Amsterdam, 1971), p. 404.
[7]E. J. McGuire, Phys. Rev. A 3, 587 (1971).
[8]D. Burch and P. Richard, Phys. Rev. Lett. 25, 983 (1970).
[9]W. Brandt and S. Lundqvist, J. Quant. Spectrosc. Radiat. Transfer 7, 411 (1967).
[10]F. W. Saris, Physica (Utrecht) 52, 290 (1971).

Nuclear Magnetic Resonance on Oriented Platinum-195*m* in Iron*

F. Bacon, G. Kaindl, H.-E. Mahnke,† and D. A. Shirley
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
(Received 13 January 1972)

The magnetic hyperfine splitting of ^{195m}Pt(*Fe*) was determined by the technique of nuclear magnetic resonance on oriented nuclei as $\mu H/kI = 89.5 \pm 0.5$ MHz. With additional γ-ray anisotropy data for the 129- and 99-keV γ rays, we derived the spin, $I = \frac{13}{2}$, and the magnetic moment of the isomeric state, $\mu(\frac{13}{2}) = \pm (0.597 \pm 0.015)\mu_N$, as well as the $E2/M1$ mixing ratio of the 99-keV γ transition, $\delta = -0.16 \pm 0.02$.

Nuclear magnetic resonance on oriented nuclei (NMR-ON)[1] provides precise information on the magnetic splitting of nuclear sublevels ($\mu H_{\mathrm{eff}}/I$). On the other hand, the magnetic hyperfine interaction (μH_{eff}) results from an analysis of the temperature dependence of γ-ray anisotropies. By a combination of both measurements the spin of the nuclear state can therefore be obtained directly. The present paper reports on the first application of this method to an isomeric state in determining the spin of the 259-keV state ($T_{1/2} = 4.1d$) of ^{195}Pt. In addition, the magnetic moment of the isomeric state and the mixing ratio of the 98.8-keV γ transition of ^{195}Pt were derived.

The ^{195m}Pt activity was produced by neutron irradiation of 57%-enriched ^{194}Pt metal in a neutron flux of 2.5×10^{15} n/cm^2 sec. Samples containing 1-at.% Pt in an iron matrix were prepared by melting the ^{195m}Pt activity under a hydrogen atmosphere with high-purity iron, already containing a matched amount of ^{60}Co activity to be used for thermometry. Thin foils (~ 20 000 Å thick), produced by cold rolling and annealing, were attached to both sides of the Cu fin of an adiabatic demagnetization apparatus. γ-ray spectra were taken at 0 and 90 deg relative to the external polarizing field H_{ext} with high-resolution coaxial Ge(Li) diodes. For the NMR-ON experiment an rf field H_1 was applied perpendicular to H_{ext}, and the amplitude of H_1 was measured by a pickup coil.

Figure 1 shows the results of the NMR-ON experiment, with the counting rate of the 98.8-keV γ rays, observed at 0 deg, plotted versus the rf frequency. The temperature of the sample increased during the run from $1/T = 145 \pm 5$ K^{-1} to 125 ± 5 K^{-1}, causing the sloping background noticeable in Fig. 1(b). Despite a total time span of 3.5 min between adjacent data points, the reso-

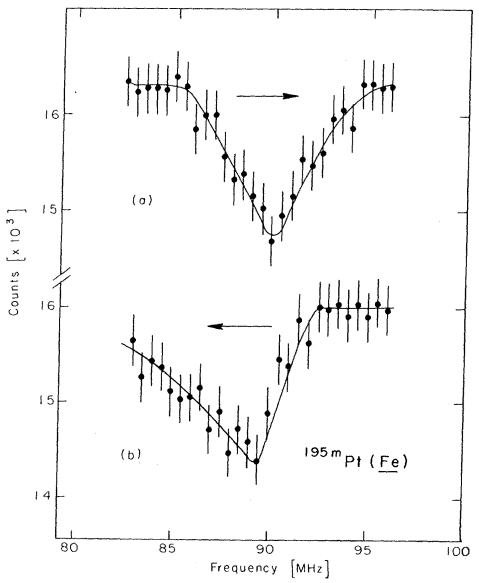

FIG. 1. Frequency dependence of the 99-keV γ-ray intensity, observed in the direction of the polarizing field $H_{\mathrm{ext}} = 1$ kOe, for (a) increasing and (b) decreasing frequency. The rf frequency was modulated with 100 Hz over a bandwidth of 1 MHz, and the rf amplitude was ~ 0.8 Oe. The time span between neighboring points is 3.5 min.