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Molecular-orbital x rays*

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Line-broadening theory is applied to photons emitted during atomic collisions. The maximum cross section for such collisions has an order of magnitude of $10^{-5}\ \pi a_0^2$, and is independent of the atomic number Z. Excitation of such radiation without the presence of atomic x rays is discussed. The spectrum may show an oscillatory energy dependence. The molecular-orbital x ray may have a linelike emission which is characteristic of the united atom.

In the electron-promotion model,[1-3] excitation of inner-shell electrons occurs in slow atomic collisions through the promotion of molecular orbitals[4,5] in passing from the separated-atoms (SA) to united-atom (UA) limit. On the basis of this model, Saris[6] discussed "molecular-orbital x rays" (MO x rays) which consist of emitted photons caused by a transition between two MO's of the molecular-collision complex. He postulated a two-step excitation mechanism. An inner-shell vacancy is produced in the projectile in a first collision with an atom. In a solid target, it is possible for a second collision to occur before the inner-shell vacancy has decayed. Because of electron promotion, the MO x ray can have a larger energy than the x ray of the SA. There are several experimental reports of such MO x rays.[7-12] Some authors[10,12] have proposed a one-step mechanism in which both excitation and x-ray emission occur during the same collision.

A troublesome feature is the continuous nature of the spectrum, which blends into the background radiation and often is dominated by strong lines of the SA. The purpose of this paper is to point out certain possibilities which could make identification of the MO x rays less ambiguous.

The theory of atomic line broadening is applicable to MO x rays. Lorentz[13] treated line broadening by considering the Fourier analysis of a classical oscillator with phase interruptions caused by collisions. Weisskopf[14] and Margenau[15] kept the concept of the Fourier analysis of the emitted wave and took into account the shifts of the atomic energy levels during the collision. Application of this approach to MO x rays leads to several immediate conclusions. The emission spectrum is simply obtained in a classical approximation by taking the separation between MO's at each time, multiplying by the emitted intensity, and integrating this result throughout the collision. Choice of large-angle scattering of projectiles leads to (1) a spectrum with a linelike feature associated with the classical turning point of the radial motion. This effect can be quite strong in heavy systems.[9,10]

A quantum-mechanical treatment can be shown to add two effects: (2) Heisenberg (uncertainty principle, $\Delta E \Delta t \sim \hbar$) broadening of the MO x ray occurs at small impact parameters and large velocities[8]; (3) an oscillatory spectrum results from interference between radiation emitted from two or more points on the trajectory followed during the collision.

The purpose of this paper is to point out via examples how these effects could bear on current experimental efforts in this rapidly developing field.

Molecular emission during collisions must be almost universal. Very often, there is at least one molecular state which is excited during the collision and which can radiate to a lower state. An important example is a symmetric ion-atom collision, which involves a mixture of at least one pair of even (g) and odd (u) states, with an allowed transition occurring between them. Examples are H^+ on H, He^+ on He, Li^+ on Li, Ne^+ on Ne, etc. MO x rays can occur if the ion is He^+ on He or Li^{++} on Li ($2p\sigma \rightarrow 1s\sigma$), Ne^+ on Ne, or Ar^{9+} on Ar ($3d\sigma \rightarrow 2p\pi$, $3d\pi \rightarrow 2p\pi$). These collisions produce inner-shell vacancies of the molecular complex during the purely adiabatic collision, but neither SA is excited either before or after the encounter. Such a collision has the advantage of eliminating or minimizing the background of SA x rays. It is important to point out that such highly stripped projectiles may occur inside thick solid targets as a result of multiple collisions.

A second feature of MO x rays is the universal magnitude of the cross section. Consider an x ray produced in a transition between the $2p\sigma \rightarrow 1s\sigma$ MO's in a proton-hydrogen collision, which has He^+ as the UA. Since radiation is most likely when the collision time is long, the maximum cross section occurs for the minimum projectile energy (~1 a.u.), just enough to form the molecular com-

plex. The radiative cross section is $\sigma \sim \pi a_0^2 (T/\tau)$, where T is the collision time, $T \sim 2a_0/v$, and $\tau \sim \tau(\mathrm{He}^+, 2p) \approx 10^{-10}$ sec is the lifetime of the $2p\sigma$ MO. This gives a radiative cross section $\sigma \sim 10^{-5}\ \pi a_0^2 \sim 10^{-21}$ cm^2. It is readily shown that, for heavier partners, this result scales in such a way to be independent of the atomic number Z. Thus, as the atomic number increases, the MO x-ray cross section should increase relative to the atomic x-ray cross sections. For $Z_{UA} \sim 1/\alpha \sim 137$, for a $1s\sigma$ vacancy, the two cross sections become of the same order of magnitude, as the probability for radiative decay during the collision approaches unity.[16]

At present, the best tests of the theory come from a comparison of the cutoff wavelength of the MO x-ray continuum with the expected separation between MO's at the distance of closest approach. Figure 1 shows such a plot for the MO x ray in collisions of carbon ions with carbon solids, taken by MacDonald *et al.*[11] The theoretical $1s\sigma$-$2p\sigma$ splittings were obtained by the scaling procedure of Briggs and Macek.[17] The agreement is reasonably good, if one allows for multiple

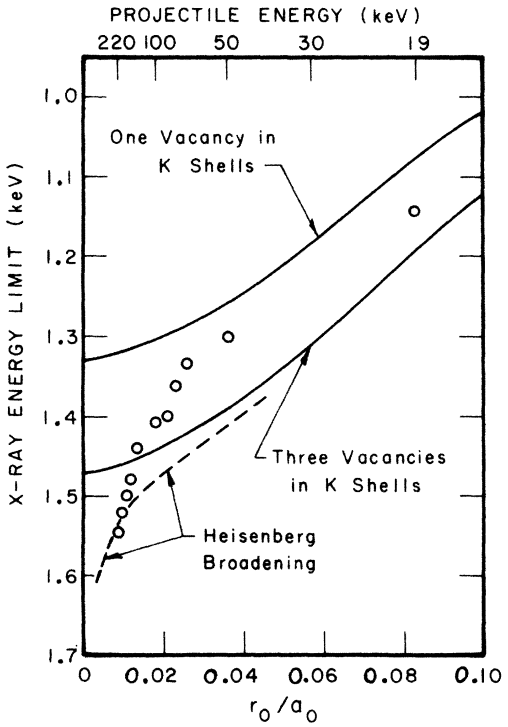

FIG. 1. Comparison of experimental x-ray cutoff energies (from Ref. 11) with estimated energies [from scaled energy levels (Ref. 17)] in the C-C$^+$ system. An error in the horizontal scale in Ref. 11 has been corrected. The Heisenberg broadening is a rough estimate based on the uncertainty principle and should not be taken as quantitatively correct.

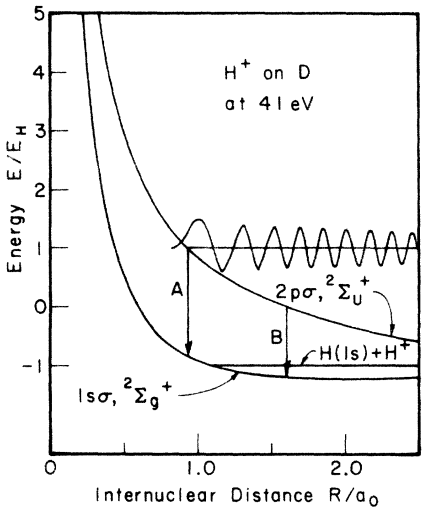

FIG. 2. Energy levels involved in radiation during collisions between a proton and a deuterium atom. The vibrational wave function of the upper state is shown. The line marked "*A*" corresponds to a transition at the classical turning point for an ion energy of 41 eV (1 a.u. in the center-of-mass frame). The line marked *B* shows a transition at a lower photon energy.

K-shell vacancies and Heisenberg broadening.[17]

In the case of coincidences between scattered particles and x rays, it is possible to select collisions where there is little or no excitation of SA. In the examples that follow, there is a head-on collision (zero impact parameter) without excitation of the *K* shell via rotational coupling of the $2p\sigma$ and $2p\pi$ MO's.

Figure 2 shows the potential-energy curves, energy levels, and upper-state vibrational wave functions involved in a head-on collision between

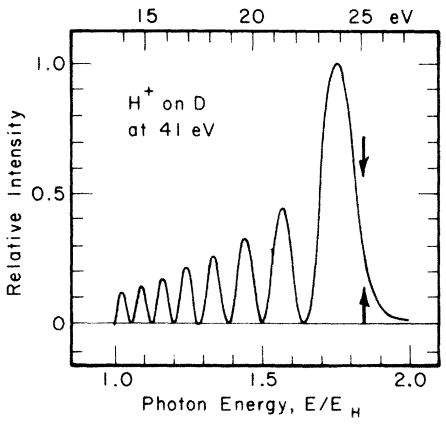

FIG. 3. Spectral energy distribution for proton-deuterium collisions. Because of the approximations used, effects caused by the vibrational structure in the lower state are ignored. The classical turning point is shown by arrows.

a proton and a deuterium atom.

Figure 3 shows calculated spectra for the proton-deuterium head-on collision, at 1 a.u. of kinetic energy (27.2 eV) in the center-of-mass frame. Figure 4 shows a similar result for C^{5+} on C with the kinetic energy properly scaled to $6^3 = 216$ a.u. in the center-of-mass frame. In calculating these curves the δ-function approximation[18] is used for the lower-state vibrational wave function. Thus effects of radiative recombination on the spectrum are ignored.[19] Correct lower-state vibrational wave functions would give a Heisenberg broadening which also is ignored here.

It can be shown that, in this approximation, the intensity I is given by the expression

$$\frac{dI}{dE} \propto \frac{\psi^2(r[E])R^2(r)E^4(r)}{dE/dr},$$

where $\psi(r[E])$ is the vibrational wave function of the upper state, r is the internuclear separation, $R(r)$ is the transition matrix element, and E is the transition energy. All these quantities are well known or easily calculated for the $2p\sigma$-$1s\sigma$ transition in H_2^+.[20]

The vibrational wave function for the upper state is calculated by means of the Airy function[21,22] near the turning point and by the JWKB approximation[21] elsewhere.

The large intensity near the turning point (Figs. 3 and 4) is a purely classical effect. The oscillations in the spectrum correspond to the peaks and valleys in the upper-state wave function (Fig. 2). Note, that in the heavier system, the spectrum is crowded together into a relatively smaller energy range. Heisenberg broadening or finite instrumental resolution would possibly wash out the oscillations in heavy systems and produce a single x-ray line. The energy of such a line is readily calculated from the UA x-ray energy levels, or more accurately, by scaling the one-electron energy levels.[17] Only about one in 10^6 collisions will result in radiation of the spectrum shown in Figs. 3 and 4.

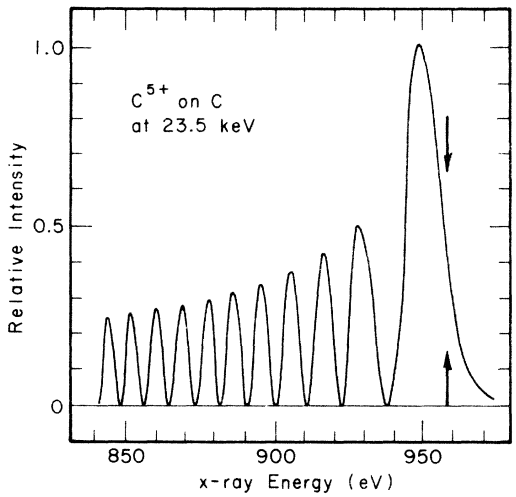

FIG. 4. Spectral energy distribution for C^{5+} on C at 23.5 keV (6^3 a.u. in the center-of-mass frame of reference). Note that the energy scale is greatly expanded. The classical turning point is shown by arrows.

The author is indebted to Jack Greenberg for reading and criticizing this manuscript.

Note added in proof. J. H. Macek and J. S. Briggs have just sent me an unpublished paper which is in agreement with the present paper and is done in more detail. In particular, by doing a fourier analysis of the emitted wave, they have treated the uncertainty broadening quantitatively.

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[2]W. Lichten, Phys. Rev. 164, 131 (1967).

[3]M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972). There are the following errors in this paper: in footnotes 23, 24, 31, 34, and 35 all references to *VIIth ICPEAC* should refer to *Abstracts of Papers of the VIIth ICPEAC* (North-Holland, Amsterdam, 1971). Allen Lurio has kindly informed me that expression (6) is only true for even values of m_l (σ, δ, γ, etc., states). Expression (6) should be reversed for odd m_l (π, ϕ, etc., states).

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Little, B. B. Triplett, and L. F. Chase, Jr., Phys. Rev. Lett. 30, 1279 (1973). W. E. Meyerhof has informed me that the MO x rays can now be accounted for within the two-step mechanism, in agreement with the promotion model. The reason for the lack of one-step mechanisms in K-shell excitation is the smallness of all couplings by nuclear motion of the $1s\sigma_g$ MO to other MO's. The only coupling that appears to be sizable is that of $1s\sigma$ to $2p\sigma$ in asymmetric collisions via a quasiresonant charge exchange. This leads to excitation of SA K-shell x rays, but not to MO x rays.

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