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High-energy dependence of the molecular-hydrogen photoionization cross section

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(Received 31 December 1973)

The photoionization cross section for H_2 per atom has recently been reported to be ~45% larger than the atomic cross section at energies of 5.41 and 8.39 keV. This note relates this observation to the differences in electron density at the nucleus in atomic and molecular hydrogen and points out that the enhancement at high photon energies is unique for molecular hydrogen.

In a recent paper Crasemann *et al.*[1] have made a careful measurement of the photoelectric cross section of molecular hydrogen at energies of 5.41 and 8.39 keV and have shown that the molecular cross section per atom exceeds the atomic-hydrogen cross section by approximately 45% at these energies. This result is at first surprising since typically at energies of 5 keV or greater above an absorption edge, photoeffect is basically an atomic process[2] and one might expect the cross section per atom for H_2 to be the same as for atomic hydrogen within the accuracy of the measurement (~7%). The purpose of this note is to explain this effect and to point out that deviations of this type are only to be expected for molecular hydrogen.

The physical reasons for the experimental findings can be understood by the following arguments. At moderately high energies the important regions of configuration space for the H_2 photoeffect will be those close to each nucleus. The reason for this is that, as discussed by Pratt,[3] the momentum transfer factor $e^{i\vec{q}\cdot\vec{r}}$, which appears in the photoeffect matrix element evaluated in the Born approximation provides an effective cutoff at distances of $r \sim 1/q$ from each nucleus. Within this framework we expect the cross section for molecular hydrogen to be additive at moderately high energies, i.e., to be due to two noninterfering (and identical) contributions whose matrix elements are large only in the vicinity of each nucleus. However, the two contributions will not be simply those that one would obtain from a calculation of the atomic-hydrogen photoeffect. The reason for this is, as will be shown, that the bound-state normalization near the nuclei are significantly different in atomic and molecular hydrogen.

The above points can be put on a more quantitative basis as follows. If we ignore any interference effects in molecular photoionization the cross section/atom may then be evaluated in exactly the same way as for an atomic system by forming the photoeffect matrix element using one nucleus as the center of coordinates. It is important to note that this procedure does not treat the photoeffect as a single-electron process. The two-electron wave functions used to describe the system in initial and final states may include electron correlation effects or allow for two-electron excitation in the photoabsorption process. The only approximation made is that there is no phase coherence of the contributions from the two atomic centers.

At energies in the region of 5–10 keV it is possible to obtain an estimate of the photoeffect cross section for molecular hydrogen without resorting to a detailed calculation. At these energies deviations due to relativistic and retardation effects should be well below the 1% level but the energy is high enough to use an asymptotic representation for the cross section. The nonrelativistic dipole-approximation high-energy asymptotic form of the cross section for a two-electron system has been derived previously[4] and is given by the relation

$$\sigma = CZ^2\delta^3(\vec{r}_1)\epsilon^{-7/2}, \tag{1}$$

where $\delta^3(\vec{r}_1)$ is a measure of the initial-state charge density of a single electron at the nucleus and ϵ is either the photon or electron energy. For a single-electron hydrogen-like system, the asymptotic form will also be given by Eq. (1).[5] Therefore, the ratio of the molecular cross section at high energies/atom to the atomic cross section will be given simply by the ratio

$$\delta^3_{\mathrm{H}_2}(\vec{r}_{1a})/\delta^3_{\mathrm{H}}(\vec{r}_1),$$

where $\vec{r}_{1a}$ refers to one hydrogen nucleus. For atomic hydrogen $\delta^3_{\mathrm{H}}(\vec{r}_1)=1/\pi$ (in a.u.). The corresponding quantity for molecular hydrogen obtained from the best available ground-state calculation[6] is found to be 0.4598. The ratio 1.444 indicates that if the asymptotic form is valid the molecular cross section/atom should exceed the atomic cross section by approximately 44% in excellent agreement with the experiment of Ref. 1 which yields $44\pm8\%$ and $45\pm7\%$ increases at 5.41 and 8.39 keV, respectively.

Recently rather detailed calculations of molecular-hydrogen photoeffect have been performed by Kaplan and Markin.[7] Their results confirm the expectation that coherence effects are unimportant at energies above 1 keV although they will be important at lower energies. Their calculations also demonstrate the enhancement of the molecular photoeffect at high energies owing to excess charge at the nucleus. However, their work appears to overestimate the cross sections at high energies, presumably owing to the failure of the Heitler-London-type wave function, used for the H_2 ground state, to provide an accurate description of the charge density near the nucleus. Their calculations also indicate that an appreciable fraction (~20%) of the photoeffect at high energies results in dissociation since they do photoeffect calculations for formation of both ground and first excited (repulsive) states of H_2^+. Formation of excited states is automatically included in the asymptotic form given in Eq. (1) since a sum of all excited states of the ion is performed in the derivation.[4] The experiment of Ref. 1 will also include contributions from excited states since all fast electrons are collected.

The results of Ref. 1 raise the question as to whether enhancement of the photoeffect cross sections at high energies over the atomic photoeffect might be observed for other light molecules. This does not appear to be the case for the following reasons. For heavier molecules the K shell, which makes the major contribution to the photoeffect at high energies is an inner shell and thus its charge density at distances near the nucleus is relatively unaffected by molecular binding. This can be seen by comparing the nuclear-charge density in Li_2 calculated in the molecular ground state[8] (13.855 a.u.) with that of an atomic calculation[9] (13.866). The difference appears to be too small to be detectable. The same is probably true for heteronuclear molecules such as LiH since in this case the dominant cross-section contribution at high energies will be from the Li K shell and the molecular binding will have little effect on the charge density near the Li nucleus.

I would like to thank Dr. U. Fano for suggesting the subject of this note and Dr. B. Crasemann for communicating his results prior to publication.

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