PHYSICAL REVIEW A VOLUME 52, NUMBER 1 JULY 1995

Metastable-hydrogen-atom scattering by crossed beams: Total cross sections for $H^*(2s)$–Ar, Xe, and CCl_4 at thermal energies

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(Received 9 January 1995)

The collision velocity dependence of total (elastic plus radiative quenching) cross sections for metastable $2s$ state H atoms with Ar, Xe, and CCl_4 has been measured in a crossed-beam experiment, in the velocity range between 4 and 40 $\mathrm{km\,s^{-1}}$. Cross sections are obtained in well-controlled velocity and angular resolution conditions, allowing a meaningful comparison with theoretical calculations. The calculated cross sections, based on estimated potentials, are in good agreement with the experimental results and indicate that collisions in the present velocity range essentially probe the long-range van der Waals portion of both the $H^*(2s)$ and $H^*(2p)$ potentials with the target. Simple considerations indicate that previous low-resolution experiments underestimated the elastic component.

PACS number(s): 34.20.Cf, 34.50.$-$s

The metastable $H^*(2s)$ atom has an excitation energy of 10.2 eV and a lifetime, against two-photon decay to the ground state, of 0.14 s. This atom exhibits an interesting peculiarity: the $2s$ metastable state is practically degenerate with the nearby $2p$ states which are characterized by a small spin-orbit splitting, of the order of $\sim 4\times10^{-5}$ eV. This feature makes $H^*(2s)$ a very "fragile" species because it can be easily quenched by a weak electric field which causes a Stark effect mixing of the $2s$ and $2p$ states with subsequent emission of Lyman-α radiation. The quenching process can occur during a $H^*(2s)$ atom collision with an atom or a molecule. When the two collision partners approach, the mutual interaction can produce a $2s \rightarrow 2p$ transition followed by decay to the ground state. Thus the physics of $H^*(2s)$ atom collisions is characterized by two dominant and complementary processes: elastic and inelastic scattering (radiative quenching) [1–5]. Recent experiments [6] where $H^*(2s)$ atoms were produced through H_2 photodissociation by synchrotron radiation, have established that, in the case of $H^*(2s)$-H_2 collisions, other inelastic processes than radiative quenching can be present, although they represent a minor contribution.

The "fragility" of the $H^*(2s)$ atom makes molecular-beam studies of this species very difficult. This explains why, in spite of its fundamental importance, only a low number of papers on metastable-hydrogen-atom collisions has appeared in the literature. In 1950 Lamb and Retherford [7] reported the first thermal-energy molecular-beam study of $H^*(2s)$, which led to the determination of very important and fundamental spectroscopic characteristics. Since then, only a few molecular-beam collision studies [1–5] involving $H^*(2s)$ atoms at thermal energy have been reported. Total and radiative quenching cross sections have been measured as a function of collision energy in the range 0.05–10 eV. It was observed that total and radiative quenching cross sections show the same collision energy dependence: this led to the conclusion that total and quenching cross sections coincide. Other measurements of the two cross sections by Dose and Richard [3] indicated that the radiative quenching cross section is approximately 80% of the total one. However, in these studies total cross sections were determined by the measurement of the $H^*(2s)$ beam attenuation when passing through a background target gas, using an experimental configuration characterized by a detector with a large acceptance angle. Under these experimental conditions only "effective" total cross sections can be measured and elastic scattering can be strongly underestimated. Integral total cross sections are correctly measured only when the collision zone is well defined and the detector acceptance angle is lower than the so-called critical minimum angle [13]

$$\vartheta_{\min} \cong k^{-1}\left[\frac{2\pi}{\sigma_{\text{tot}}}\right]^{1/2},$$

where k is the wave number, $k \equiv \mu v/\hbar$, with μ the reduced mass and v the asymptotic relative collision velocity.

Various theoretical approaches to the collisional quenching cross sections have been reported [8–10]. Quenching cross sections have been calculated by Byron and Gersten [10] through an impact-parameter approach by the use of perturbation theory, while Slocomb, Miller, and Schafer [9] have employed a two-state-resonance model, with a formalism identical to that used for symmetric charge transfer. This approach requires the knowledge of the $H^*(2s)$ and $H^*(2p)$ interaction potentials with the target and has been applied only to the case of helium [9]. The elastic counterpart of metastable $H^*(2s)$ atom collisions has received much less attention. By the use of the two-state-resonance model the calculation of total cross sections, that is, elastic plus quenching cross sections, is possible. Nevertheless, a comparison

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between experimental and theoretical total cross sections has never so far been attempted.

In this Brief Report a crossed-beam study of H*(2s) atom collisions with Ar, Xe, and CCl_4 is reported. The velocity dependence of the total integral cross section has been measured in the thermal-velocity range (from 4 to 40 $km\,s^{-1}$) by the use of an experimental configuration such that the detector acceptance angle is well below the minimum critical angle. The cross sections are calculated in terms of the two-state-resonance model and compared with experimental results. It is shown that the total scattering at these experimental velocities is mainly determined by the long-range van der Waals portion of both H*(2s) and H*(2p) Σ-character potentials with the target. Simple theoretical considerations, based on this result, explain the previous observation [11] that total and quenching cross sections exhibit the same average energy dependence and indicate that previous "effective" total cross section measurements underestimated the elastic component.

Integral total cross sections have been determined by measuring the attenuation of a velocity-selected H*(2s) beam when crossing a secondary target beam. The experimental setup is schematically shown in Fig. 1. H*(2s) atoms are produced by electron bombardment of a H_2 molecule beam, in a source similar to that previously used by Baudon and co-workers [5]. The bombarding electrons are pulsed in order to have an excited-atom beam suitable for time-of-flight (TOF) velocity analysis. The electron impact occurs in a field-free region, shielded by a grounded copper tube. The target-beam source consists of a glass microcapillary array which produces a beam at a right angle with respect to the excited-atom beam. The detector is a quencher of H*(2s) atoms and is based on the design proposed by Czuchlewski, Ryan, and Wing [12].

For TOF spectrum measurements, the detector is connected with an ORTEC ACE-MCS unit driven by a PS IBM system. The collision velocity dependence of the total cross section has been obtained by measuring TOF spectra with and without target molecules in the scattering volume. Typical metastable TOF spectra are also shown in Fig. 1. The spectra show two maxima, for ~10 and ~40 km/s atom velocity, which come from two dissociative channels of H_2 excited by electron bombardment [1].

The detector acceptance angle in the present arrangement was ~0.01 rad, which is smaller than the critical minimum angle $\vartheta_{\min}$ for all the investigated system in the full collision velocity range. The TOF velocity-selected excited-hydrogen-atom beam intersects an effusive target molecular beam at right angles, rather than gas molecules in a collision cell or background gas, as done in previous experiments. This method produces a better definition of the relative velocity, since it removes the averaging inherent in the isotropic velocity distribution of a static gas. The effect of the target-molecule velocity spread has been taken into account during the analysis. However, due to the large masses of the targets used a significant effect is present only at low collision velocities.

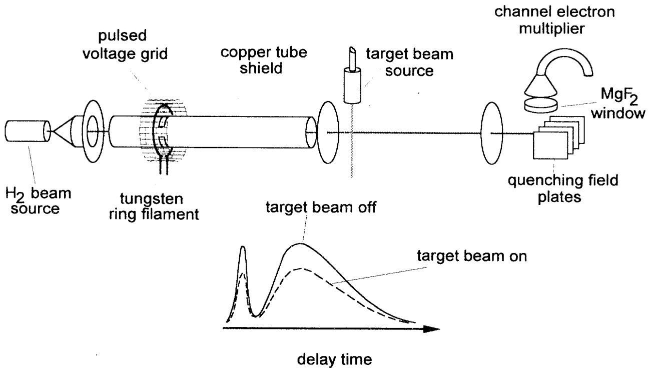

FIG. 1. A schematic view of the experimental setup. A typical time-of-flight spectrum of the H*(2s) beam with and without the target-molecule beam is also shown.

The measured integral total cross sections are reported in Fig. 2. Two groups of data points appear for each system, corresponding to the two maxima in the H* velocity distribution. The cross sections for all the systems show a decreasing trend with increasing velocity. The cross sections for H*(2s)-CCl_4 have been studied here because this molecule is symmetric and with such a large polarizability that a glory interference structure [18] is expected in the low-velocity region. Such a structure, due to quantum-mechanical interference between particles undeflected because of a balance of long-range attraction and short-range repulsion, does appear in our results as a typical undulatory velocity dependence of the integral cross section.

The experimental results can be interpreted by the following considerations. One has to take into account that

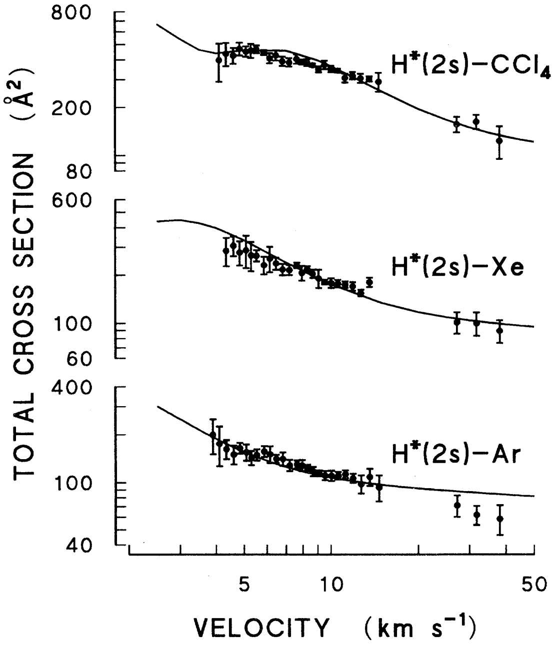

FIG. 2. The collision velocity dependence of the total scattering cross sections for H*(2s) interacting with Ar, Xe, and CCl_4. The full lines are theoretical calculations, while the dots are the experimental results normalized to the theoretical values.

the Σ-symmetry interaction potential for the H*(2s)–rare-gas-atom system is asymptotically degenerate with the two potentials for the H*(2p) system, one of Σ and the other of Π symmetry. Since Σ-Π transitions can here be neglected [9], the collision can be treated as a two-state-resonance case, where only the two $^2\Sigma$ states correlating with H*(2s) and H*(2p) are taken into account. Within this assumption, equations identical to those used in symmetric charge-exchange processes [14] apply. The $2s\rightarrow2p$ cross section is then given by

$$\sigma_{2s\rightarrow2p}=\frac{\pi}{k^2}\sum_l(2l+1)\sin^2(\eta_l^{2s}-\eta_l^{2p})\ , \tag{1}$$

while the elastic $2s\rightarrow2s$ cross section is

$$\sigma_{2s\rightarrow2s}=\frac{\pi}{k^2}\sum_l(2l+1)[2\sin^2\eta_l^{2s}+2\sin^2\eta_l^{2p}-\sin^2(\eta_l^{2s}-\eta_l^{2p})]\ . \tag{2}$$

The total scattering cross section, which we have measured, is therefore

$$\sigma_{\mathrm{tot}}=\frac{2\pi}{k^2}\sum_l(2l+1)[\sin^2\eta_l^{2s}+\sin^2\eta_l^{2p}]\ , \tag{3}$$

where η_l^{2s} and η_l^{2p} are the phase shifts for the two curves, of Σ symmetry, correlating with 2s and 2p states, respectively.

The interaction potentials of H*(2s) and H*(2p) with the targets have not been characterized previously, except for the case of the short-distance interaction of H*(2s)-Ar [15]. As a first approach a semiempirical estimate has been attempted according to the following considerations. The interaction between a metastable H* and a closed-shell atom or molecule M is characterized by a van der Waals weak interaction at long distances, while at short range the interaction is mainly determined by the Rydberg-state molecule given by an $M\mathrm{H}^+$ core surrounded by an excited electron. This is analogous to the case of the rare-gas metastable atoms [16]. By assuming that in the present collision energy range only long-range distances are probed, where the van der Waals component is dominant, a calculation has been performed by using the potential parameters obtained, following Pirani and co-workers [17], starting from the polarizabilities of the collision partners. The parameters are reported in Table I. It has to be noted that the different polarizabilities of the H atom in the 2s and 2p (Σ symmetry) states lead to sensibly different long-range Van der Waals interactions. The total cross sections have been calculated by the use, in all cases, of simple Lennard-Jones (12,6) potentials splined to a long-range $-C_6/R^6$ attraction and computing the phase shifts within the JWKB approximation. The center-of-mass total cross sections σ_{tot} have then been convoluted over the experimental velocity resolution.

A comparison between experimental and calculated cross sections is shown in Fig. 2, where the relative experimental results are reported normalized to the absolute theoretical values. The agreement between experimental and theoretical trends is fairly good, indicating that total cross sections, in the investigated velocity range, are indeed essentially dominated by the long-range van der Waals forces. However, the experimental results at high velocity for the argon case deviate significantly from theoretical results. For such a system and in that velocity range the critical minimum angle becomes comparable with the detector acceptance angle, making the comparison between theoretical and experimental data less reliable.

TABLE I. Potential parameters for $n=2$ excited hydrogen atoms interacting with Ar, Xe, and CCl$_4$. ε and R_m are, respectively, the energy and the location of the potential minimum, while C_6 is the coefficient for the long-range $\sim R^{-6}$ attraction.

	ε (meV)	R_m (Å)	C_6 (meV Å^6)
H(2s)-Ar	6.00	4.55	7.41×10^4
H(2p)-Ar[a]	5.25	4.92	1.03×10^5
H(2s)-Xe	12.0	4.69	1.77×10^5
H(2p)-Xe[a]	11.5	5.00	2.48×10^5
H(2s)-CCl$_4$	21.9	4.96	4.50×10^5
H(2p)-CCl$_4$[a]	23.1	5.20	6.35×10^5

[a] Σ symmetry.

It is well established from elastic-scattering studies of atom-atom collisions [18] that the total cross section exhibits an oscillatory behavior superimposed over a monotonic trend which is mainly responsible for the size of the cross section. Such a trend is determined by the long-range attraction, and in the case of a $\sim R^{-s}$ attraction can be easily evaluated by the use of the Schiff-Landau-Lifschitz formula [19,20]. Following the same treatment used to obtain such a formula in the case of a $-C_6/R^6$ long-range attraction, we have obtained the following relationships for the monotonic component of the total cross section of Eq. (3):

$$\sigma_{\mathrm{tot}}\approx\frac{g(6)}{2(\hbar v)^{2/5}}(C_{2s}^{2/5}+C_{2p}^{2/5})\ , \tag{4}$$

and of the inelastic cross section of Eq. (1):

$$\sigma_{2s\rightarrow2p}\approx\frac{g(6)}{4(\hbar v)^{2/5}}(C_{2s}-C_{2p})^{2/5}\ , \tag{5}$$

where $g(s)$ is a known function with $g(6)=8.083$ [18]. C_{2s} and C_{2p} are the long-range C_6 coefficients for the H*(2s) and H*(2p) Σ-symmetry interactions reported in Table I.

Some interesting considerations can be drawn from relationships (4) and (5). They show that the monotonic trend of total and quenching cross sections must have the same $\sim v^{-2/5}$ dependence. This explains the previous observation [2,3] that total and radiative quenching cross sections exhibit the same velocity dependence. Moreover, they indicate that $\sigma_{2s\rightarrow2p}/\sigma_{\mathrm{tot}}$ is $\sim\frac{1}{6}$ for all investigated systems. This is in contrast with previous determinations [3], but, as discussed above, "effective" total cross section measurements can strongly underestimate the elastic components. On the other hand, radiative cross section, $\sigma_{2s\rightarrow2p}$, values have been measured by Dose and Richard [3] for the argon case and these are in good agreement with the prevision of relationship (5). This last observation indirectly confirms the validity of the approximate formulas (5) and (6) and suggests again that in previous experiments the elastic component was underestimated.

In conclusion, we have performed the measurement of total integral cross sections for metastable $H^*(2s)$ atom collisions, by using a detector characterized by an acceptance angle lower than the minimum critical angle. This has allowed a comparison between experimental and theoretical cross sections. It has been found that collisions in the present energy range essentially probe the long-range van der Waals portion of both $H^*(2s)$ and $H^*(2p)$ Σ-symmetry interaction potentials with the targets. The previous experimental observation that total and radiative quenching cross sections show a similar energy dependence is explained. Serious doubts are cast on the previously determined relative size of total and radiative quenching cross sections. Further information will come from the measurement of radiative quenching cross sections in the same experimental conditions. Also, measurements of total cross sections will be extended to lower collision velocities where glory interference structures are expected.

The authors are grateful to F. Pirani and D. Cappelletti for the help in estimating the potential-energy curves. The authors also thank V. Aquilanti, J. Baudon, J. M. Farrar, and E. Nikitin for useful discussions. M.P.M. wishes to thank the Ministerio de Educacion y Ciencia of Spain for financial support. Financial support from the EEC Science Program, CNR bilateral agreement, and a NATO Grant for International Collaboration is gratefully acknowledged.

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