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Autoionization electrons following double excitation of D_2 in 2.4 keV $e^- + D_2$ collisions: Experimental and theoretical evidence

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The electron spectra originating from ionization of D_2 by impact of 2.4 keV electrons have been measured at various emission angles. After subtraction of the direct ionization background, three peaks are clearly visible in the electron energy range 1–20 eV. The existence of these peaks is confirmed by theoretical calculations. Two of these peaks are due to autoionization of doubly excited states lying above the first and second ionization thresholds. The third peak is attributed to the strong interference between direct ionization and autoionization while the molecule is already dissociating.

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Among the multiple processes that occur in collisions of photons or ionized particles on H_2 and D_2 targets, double excitation (DE) has been the subject of many experimental [1–6] and theoretical [7–12] works during the last thirty years. Doubly excited states (DES) of H_2 or D_2 following photon or electron impact are known to play an important role as intermediate resonant states in a wide range of atomic and molecular processes occurring in plasma physics, laser physics, and astrophysics. The formation of these states in collisions of charged particles with H_2 or D_2 is of particular interest because a large number of exit channels is involved, especially at low impact velocities [13,14].

In this work, we consider the case of the D_2 target. Figure 1 shows the potential energy curves of some relevant DES of D_2 [12,15]. The Q_1 DES of D_2 lie above the first ionization threshold [the $X^2\Sigma_g^+(1s\sigma_g)$ state of D_2^+] and may autoionize leading either to (i) a bound molecular ion D_2^+ (arrows in Fig. 1) or to (ii) a neutral atomic deuterium plus a deuteron (dissociative ionization). Process (ii) is possible when most excitation energy is taken by the nuclei instead of by the ejected electron. In this case, the electron kinetic energy is smaller than in process (i). Moreover, Fig. 1 shows that these DES curves cross the ionization threshold at large internuclear distances ($>$3.5 a.u.) and, therefore, they no longer autoionize in that region. Thus, if the autoionization lifetime is long enough, these states may lead to (iii) dissociation of the molecule into two neutral deuterium atoms instead of to ionization. The latter process, called resonant dissociation, competes efficiently with processes (i) and (ii) [11], but does not lead to electron emission. This means that autoionization can only be observed for those states that autoionize before process (iii) occurs. If the autoionization lifetime is very short, the DES will decay in the Franck-Condon region (the dotted lines in Fig. 1), but this is not the case in general [11].

Figure 1 also shows the Q_2 DES lying above the second ionization threshold $^2\Sigma_u^+(2p\sigma_u)$. These states may decay by autoionization either to the first or to the second ionization threshold. Thus, if e.g., autoionization occurs in the Franck-Condon region, these states lead to slow ($<$5 eV) or fast ($\sim$5–20 eV) electrons corresponding to autoionization through the $^2\Sigma_u^+(2p\sigma_u)$ or $X\,^2\Sigma_g^+(1s\sigma_g)$ thresholds, respectively. As for the Q_1 states, processes (ii) and (iii) are also possible.

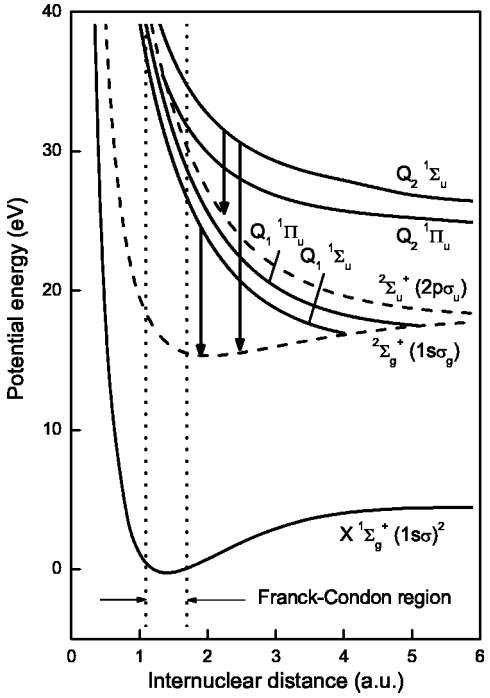

FIG. 1. Potential energy diagram for D_2. The single-electron (dashed lines) and double-electron (full lines) excited states are taken from Refs. [18,23]. The arrows indicate the possible autoionization channels following the double excitation process.

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As mentioned above, in addition to autoionization, DE of D_2 (and H_2) leads to the ejection of deuterons (protons) and/or excited neutral atoms. Hence, to investigate the DES of H_2 and D_2, most previous experimental studies focused on the analysis of both the fragment kinetic energy distributions [5,6] and the photons emitted by the excited fragments [2,4]. From these studies, qualitative information on the energy positions of these states has been obtained. An estimate of autoionization widths as functions of internuclear separation has been obtained for the lowest DES from the proton/deuteron ratio in dissociative photoionization of H_2 and D_2 [5]. Also, the relative importance of partial autoionization widths corresponding to different ionization thresholds has been determined [6]. Nevertheless, experimental data for resonance parameters (i.e., autoionization energies and lifetimes) are still very scarce, mainly due to the existence of strong interferences between (i), (ii) and (iii) [16] that complicate the analysis. Hence, most of the information about DES of H_2 and D_2 comes from theoretical works [7,9,11,12,15,17].

The observation of autoionization electrons by electron spectroscopy should bring additional and more direct information about the properties of DES. This is an experimental challenge. First of all, because electrons associated with the DE process are much less abundant than those originating from the dominant direct ionization (DI) process. Secondly, because the nuclear motion smoothes all resonance peaks associated with the DE process [18]. These difficulties explain why previous attempts in photoionization experiments have failed in identifying autoionization electrons [19,20]. Very recently, the presence of these electrons has been suggested in electron spectra following 68 MeV/u $Kr^{33+}+H_2$ collisions [21], however no definite conclusion could be obtained because resonance peaks were absent at several observation angles. Thus, observation of autoionization electrons still remains an open problem.

In this paper we present the first clear evidence of autoionization electrons following DE of D_2 after impact of 2.4 keV electrons. These electrons have been observed at angles ranging from 30° to 130°. The key point for a successful observation of autoionization electrons is to perform measurements with high statistics. This is essential to separate the corresponding signal from the background due to the dominant DI process. The detailed structure of the autoionization electron spectra is compared with theoretical calculations and the different peaks observed in the experiment are unambiguously identified. Besides providing quantitative information on autoionization of D_2 (energies and cross section), this work opens the door for future experiments in which, e.g., the energy of the autoionization electron is measured in coincidence with that of the D^+ fragment or with the Lyman-α rays emitted from excited D(nl). The latter experiments will be important to obtain direct information on energy positions and lifetimes of individual DES, which is not possible by just analyzing the energy of the D^+ fragments.

The experiment has been performed at CIRIL (Caen) using an electron gun of simple design. A beam of 2.4-keV electrons collimated to a diameter of ~2 mm was directed onto a jet of D_2 molecules. The emitted target electrons were energy analyzed using a single-stage spectrometer, which consists of a 90° parallel-plate analyzer. The voltage on the plates of the spectrometer was scanned to record the electron yields as a function of the electron emission energy, for several observation angles relative to the beam direction [22].

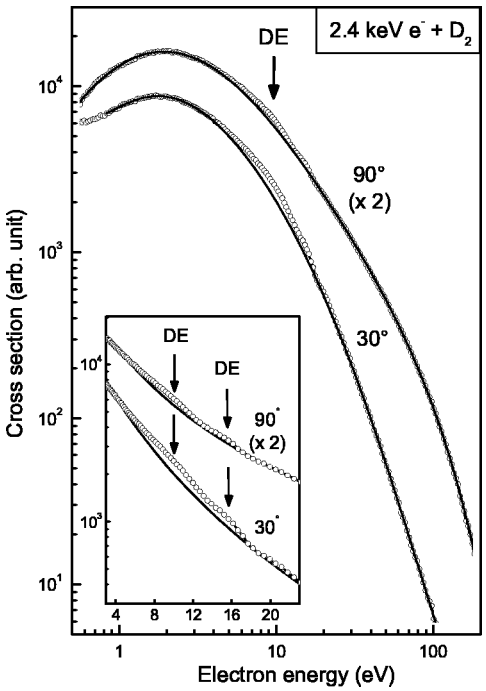

FIG. 2. Cross section for electron emission by 2.4 keV e^- impacting on D_2, as a function of the ejected electron energy, obtained at the observation angles of 30° and 90°. The full curve is a fit of the background. The arrows indicate the positions of the structures due to the autoionizing double excitation of D_2.

Figure 2 shows typical doubly differential cross section (DDCS) spectra as functions of the target electron energy for the emission angles of 30° and 90°. The electrons originate mainly from single ionization. It is seen that the cross section decreases strongly when increasing the emitted electron energy. Superimposed on the ionization spectrum, a small structure centered at ~8–10 eV is clearly observed. It was verified that this structure is not due to the excitation of spurious gases, such as N_2 or O_2. This reproducible structure is thus attributed to the double excitation of D_2. A careful inspection of the spectra (the inset of Fig. 2) reveals an additional structure at electron energies around 15 eV. Both the latter structure and the one at ~8–10 eV are systematically observed at each investigated angle.

To enhance the visibility of the DE signal, a polynomial function was used (in the logarithmic scale) to reproduce the DI contribution below 2 eV and above 20 eV. The quality of the fit was found to be practically independent of the degree of the polynomial function for degrees ranging from 4 to 7. Subtraction of this DI contribution leads to the DE spectrum, as shown in Fig. 3 for the emission angle of 90°. As mentioned above, the DE spectrum consists mainly of two peaks centered at ~8.5 eV and 15 eV. In addition, a low intense structure is also observed at electron energies lower than 5 eV. We have found that the shape of the DE spectrum is nearly independent of the observation angle within the statistical error bars.

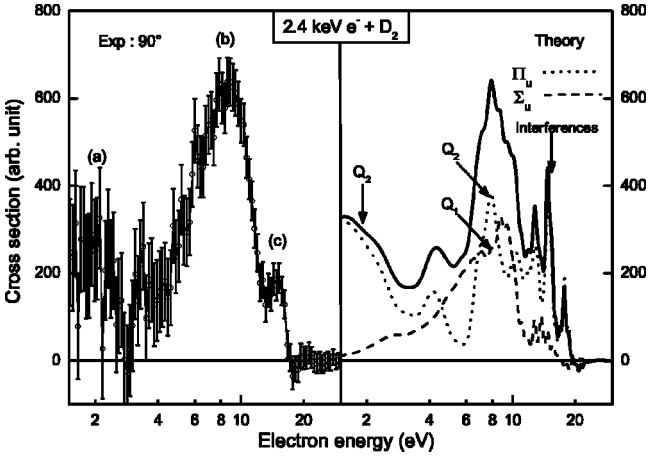

FIG. 3. Experimental (left side) and theoretical (right side) cross sections for Auger electron emission in 2.4 keV $e^- + D_2$ collisions, as a function of the ejected electron energy. Statistical error bars for the experimental data are also reported.

The whole spectrum (open circles in Fig. 2) and the direct ionization DDCS (full curves in Fig. 2) have been integrated over the emitted electron energy ϵ and the emission angle. This gives total and direct ionization cross sections σ_{tot} and σ_I, respectively. The resulting cross section σ_I was then normalized to the value of 1.0×10^{-17} cm^2 obtained by the extrapolation of previous measurements [23]. In principle, it is not possible to extract absolute DE cross sections from the difference between σ_{tot} and σ_I due to the interference between DI and autoionizing DE [24]. However, one can use this procedure to estimate the order of magnitude of the DE cross section. We have found a value of $(1.9\pm0.6)\ 10^{-19}$ cm^2, which is comparable to the value of 0.64×10^{-19} cm^2 obtained by the extrapolation of the measurements reported in [23]. This result supports the validity of our fitting procedure to determine the DI background.

The basic formalism to analyze the angular distribution of ionized electrons has been introduced in Refs. [25,26]. To our knowledge, this formalism has only been applied to evaluate photoionization cross sections, which are related to the angle integrated cross section $\sigma(\epsilon)$ through the usual formula $d\sigma/d\Omega=\sigma(\epsilon)[1+\beta(\epsilon)P_2(\cos\theta)]/(4\pi)$; θ is the emission angle. Previous photoionization experiments on H_2 [26,27] have shown that the β parameter barely depends on ϵ even in the vicinity of DES. Consequently, the $d\sigma/d\Omega$ and σ spectra are nearly identical at any angle up to a normalization factor. Since dipole transitions govern the entire spectrum at the high impact energy considered in this work ($\sim$13 a.u.), a similar behavior is expected in our experiments. As mentioned above, this is exactly what we observe.

Consequently, in order to understand the origin of the structures observed in the experiment, it is enough to consider the angle integrated cross section. The latter has been evaluated in the framework of the first Born and dipole approximations. For randomly oriented molecules, it is given by (in a.u.)

$$\sigma(\epsilon)=\frac{4(2\pi)^3\sqrt{2\epsilon}}{3v^2}\sum_{\alpha lm\mu}\int_0^{W_{\alpha v_\alpha}^{\max}}dW_{\alpha v_\alpha}\ln\left(\frac{2v^2}{\epsilon+W_{\alpha v_\alpha}}\right)\times\left|\int dR\langle\Psi^+_{\alpha v_\alpha\epsilon lmW_{\alpha v_\alpha}}|\hat{O}_\mu|\Psi_{g\nu}\rangle\right|^2, \quad (1)$$

where v is the electron impact velocity, α runs over open ionization channels, v_α is the vibrational state in channel α, $W_{\alpha v_\alpha}$ is the corresponding vibrational energy, $W^{\max}_{\alpha v_\alpha}$ is the maximum vibrational energy in channel α that is compatible with the energy of the incoming electron, l is the angular momentum of the ionized electron, m is the corresponding azimuthal quantum number, $\Psi_{g\nu}(\mathbf{r},R)$ and $\Psi^+_{\alpha v_\alpha\epsilon lmW_{\alpha v_\alpha}}(\mathbf{r},R)$ are the ground and final states of the molecule, respectively, $\mathbf{r}$ represents the electronic coordinates, R is the internuclear distance, $\hat{O}_\mu$ is the two-electron dipole operator, and $\mu=x$, y and z. The wave functions $\Psi_{g\nu}$ and $\Psi^+_{\alpha v_\alpha\epsilon lmW_{\alpha v_\alpha}}$ are evaluated in the adiabatic approximation from Eqs. (42) and (60) of Ref. [28]. Briefly, the final state $\Psi^+_{\alpha v_\alpha\varepsilon lmW_{\alpha v_\alpha}}$ results from a close coupling calculation that includes contributions from the four lowest ionization thresholds of D_2 $[X\ ^2\Sigma_g^+(1s\sigma_g), ^2\Sigma_u^+(2p\sigma_u), ^2\Pi(2p\pi_u), ^2\Sigma_g^+(2s\sigma_g)]$, the Q_1, Q_2, Q_3, and Q_4 doubly excited states, and the corresponding nuclear states that describe vibration and dissociation. Therefore, $\Psi^+_{\alpha v_\alpha\epsilon lmW_{\alpha v_\alpha}}$ is not given by the product of an electronic and a nuclear wave function and accounts for interferences among the various electronic and nuclear channels. The non resonant background has been obtained by excluding all Q states from the close coupling expansion.

The theoretical results are presented in Fig. 3 (right side), normalized to the experimental spectrum at 90° and convoluted with a Gaussian function to account for the 5% energy resolution in the experiment. The three structures observed in the experiment are also present in the calculated spectrum. More precisely, the dominant peak is centered at 8.5 eV in both spectra, and the widths are close to each other. The peak observed at $\sim$15 eV is reproduced more or less by the calculation, although the intensity is slightly larger than in the experiment. This is also the case for the structure observed at energies smaller than 5 eV. Concerning the comparison with experiment, it should be noted that, in addition to the statistical uncertainties, the DI subtraction procedure induces further uncertainties on the final DE spectra. The latter uncertainties are particularly significant ($\sim$30%) in the low energy ($<$5 eV) region. Thus, taking into account the difficulties in extracting the information from experiment, the agreement between experiment and theory is reasonably good.

The theoretical calculations allow one to understand the origin of the different peaks observed in the experiment. Figure 3 shows the contributions of the $^1\Sigma_u^+$ (dashed line) and $^1\Pi_u$ (dotted line) symmetries (these are the only symmetries allowed in the dipole approximation). Peak (a) is essentially due to autoionization of the lowest Q_2 states of $^1\Pi_u$ symmetry through the excited ionization threshold $^2\Sigma_u^+(2p\sigma_u)$. Autoionization of these states through the lowest threshold $X\ ^2\Sigma_g^+(1s\sigma_g)$ leads to a significant part of peak (b). Another important contribution to peak (b) comes from autoionization

of the Q_1 states of $^1\Sigma_u^+$ symmetry through the lowest ionization threshold $X\ ^2\Sigma_g^+(1s\sigma_g)$. In contrast, the contributions of Q_3 and Q_4 states were found to be negligible, so one can expect that a higher DES will have a minor effect. Most of the signal associated to the observed peaks correspond to *dissociative* ionization.

The origin of peak (c) is subtle. This peak appears both in the $^1\Sigma_u^+$ and $^1\Pi_u$ symmetries and results from the interference between direct ionization, autoionization and dissociation. Indeed, the autoionized electron is ejected when the two nuclei have already began to separate. This means that the interference between autoionizing DE and DI does not occur in the Franck Condon region or, equivalently, that the interference manifests at electron energies different from those corresponding to a "vertical" electron decay. The existence of strong interference effects related to molecular dissociation has been theoretically predicted [11] in the case of H_2 photoionization. The interferences are clearly visible in the kinetic energy distribution (KED) of ejected protons and explain, e.g., the presence of unexpected peaks in the spectra measured by Ito *et al.* [6] at low proton energies. Earlier experimental works [23] have not shown any evidence for this phenomenon. Thus, using a totally different approach, i.e., electron spectroscopy, we provide additional evidence for the existence of these interference effects.

In conclusion, we provide clear experimental evidence for electron emission following double excitation of D_2 by fast electron impact. Due to the high statistics of the spectra, the present results give detailed information on the energy distribution of the emitted autoionization electrons: after subtraction of the direct ionization contribution, three structures due to autoionizing double excitation are revealed at energies lower than 20 eV. Theoretical calculations show that Q_1 and Q_2 DES give the major contribution to the double excitation process. They also show that the peak observed at energies larger than $\sim$10 eV results from interference between direct ionization and autoionization while the molecule dissociates. This confirms the observations of Ito *et al.* [6] and shows that a correct assignment of the observed peaks requires the inclusion of the nuclear motion. The observation of electrons following double excitation of D_2 opens the way for a new generation of experiments in which molecular autoionization electrons (and only these electrons) are analyzed, e.g., in coincidence with heavier fragments and/or emitted photons.

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