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Symmetry breaking by quantum coherence in single electron attachment

E. Krishnakumar1*, Vaibhav S. Prabhudesai1 and Nigel J. Mason2

Quantum coherence-induced effects in atomic and molecular systems are the basis of several proposals for laser-based control of chemical reactions. So far, these rely on coherent photon beams inducing coherent reaction pathways that may interfere with one another, to achieve the desired outcome. This concept has been successfully exploited for removing the inversion symmetry in the dissociation of homonuclear diatomic molecules, but it remains to be seen if such quantum coherent effects can also be generated by the interaction of incoherent electrons with such molecules. Here we show that resonant electron attachment to H2 and the subsequent dissociation into $H(n = 2) + H^-$ is asymmetric about the inter-nuclear axis, whereas the asymmetry in $D_2$ is far less pronounced. We explain this observation as due to attachment of a single electron resulting in a coherent superposition of two resonances of opposite parity. In addition to exemplifying a new quantum coherent process, our observation of coherent quantum dynamics involves the active participation of all three electrons and two nuclei, which could provide new tools for studying electron correlations as a means to control chemical processes, and demonstrates the role of coherent effects in electron-induced chemistry.

The development of many concepts in quantum information technology depends crucially on effects induced by quantum coherence in atomic and molecular processes. Quantum coherence forms also the basis of several proposals for controlling chemical reactions using lasers, which can be achieved by exciting a molecule to a given state through more than one quantum path using coherent photon beams. To achieve the desired outcome, the ensuing interference between quantum paths can be tailored using their phase difference. One of the most fascinating effects of these schemes is the breaking of inversion symmetry in a homonuclear diatomic molecule. Since single-photon absorption is dominated by dipole transitions, breaking the inversion symmetry in a homonuclear diatomic system requires the simultaneous presence of two photon absorption paths. These coherent photon absorption paths, one of odd and the other of even parity, interfere with one another, and the interference changes with the phase difference between the two photon paths. An essential aspect of this process is the coherent transfer of odd and even angular momenta to a single molecule using two different sets of laser beams that are coherent with one another. Can such a phenomenon take place in particle collisions? In other words, will quantum coherence be observed in a particle collision when more than one angular momentum transfer channel can be accessed with comparable strength to create a situation similar to the two-photon interference process? If so, then such projectiles need not be coherent to invoke the quantum coherence in a system. Here we show that this indeed happens in the case of electron attachment to hydrogen molecules.

Resonant attachment of an electron to a molecule forming a negative ion resonance (NIR) and its subsequent decay through dissociation forming a stable negative ion and one or more neutral atoms or radicals is called dissociative attachment (DA). The process of DA in $H_2$ together with its time-reversed process of $H^-$ and $H$ combining to form a $H_2$ molecule and a free electron, known as associative detachment (AD), are important in many areas of physics and chemistry, from cosmology to the science and technology of controlled fusion. Resonant attachment is based upon the symmetry of the neutral state and the NIR that is formed. It has been shown that due to the inversion symmetry and subsequent parity conservation in homonuclear diatomic molecules such as $H_2$, capture of only odd or even partial waves (angular momentum quanta) of the incoming electron is allowed. Indeed, for a transition between states with the same parity, capture of only even values of angular momentum quanta, $l$, are allowed and for opposite parity only odd values are allowed. Also, due to the low energy of the projectiles, lower-order partial waves tend to be more dominant compared to the higher-order partial waves. Thus, in the case of $H_2$, where the molecule in the ground state has a $\Sigma^+_g$ symmetry, the formation of the NIR with $\Sigma^+_u$ symmetry allows all orientations of the molecule with respect to the incoming electron ($l = 0$ is the dominant partial wave) and the angular distribution of $H^-$ will show little if any anisotropy, as shown in Fig. 1a. Similarly, for the negative ion states $\Sigma^+_g$, $\Pi_u$ and $\Pi_u$, the angular distributions are expected to be as shown in Fig. 1b–d, respectively. In any such case, the distribution is always symmetric with respect to the direction of the electron beam. DA experiments on all the homonuclear diatomic molecules studied to date, including $H_2$ (in the limited angular range), have consistently shown this symmetry.

$H^-$ production from $H_2$ through DA appears as peaks in the cross section at 4 eV and 14 eV, and as a broad peak between 7 and 13 eV (ref. 16). The threshold for the formation of $H^-$ from $H_2$ is 3.724 eV (bond dissociation energy of $H_2 = 4.478$ eV, electron affinity of $H = 0.7545$ eV). The 4 eV resonance dissociates to yield $H_2^-(1s^2) + H$ with both fragments in their respective ground states. The broad peak between 7 eV and 13 eV is due to a purely repulsive NIR state which dissociates into the ground states of $H^-(1s^2)$ and $H(1s)$. The 14 eV peak leads to $H^-(1s^2)$ and the excited $H(n = 2)$ atom (threshold 13.92 eV), hence the fragments are formed with very low kinetic energies, similar to that of the 4 eV...
channel. H\(^-\) formation is also possible at higher electron energies, with the opening of a new channel (dipolar dissociation) that has a threshold at 17.75 eV. It has been shown that between 14 eV and the opening of a new channel (dipolar dissociation) that has a threshold, H\(^-\) formation is possible. Between 14 eV and the opening of a new channel (dipolar dissociation), H\(^-\) formation is possible.

We carried out a series of experiments to measure the angular distribution of H\(^-\) produced by the DA to H\(_{2}\) and D\(_{2}\) using the velocity slice imaging technique\(^{16}\). The details of the experimental technique are given in Methods.

Velocity slice images of H\(^-\) at 4.5 eV and 14.5 eV are shown in Figs 2a and 2b, respectively. It can be seen that the image at 4.5 eV shows a symmetric distribution in the forward and backward directions, and based on Fig. 1b, we conclude that the resonant state is of \(\Sigma^+_u\) symmetry. In contrast to the 4.5 eV image, the 14.5 eV image shows a noticeable forward-backward asymmetry. That the intensity distribution is parallel to the electron beam implies the contribution from a resonance of \(\Sigma^+_u\) symmetry. The measurements carried out at higher electron energies show a similar asymmetry in the distribution, as can be seen in Fig. 2b–d. The results for D\(_2\) in the same energy range are shown in Fig. 2e–g. While the images of H\(^-\) show a marked asymmetry, the images of D\(^-\) from D\(_2\) show much less asymmetry. The slight asymmetry that is present in the D\(^-\) image appears to change direction with electron energy—at 14 eV the asymmetry is opposite to that seen in H\(_2\), at 14.5 eV the distribution is almost symmetrical, and at 15 eV it is in the same direction as that in H\(_2\).

As discussed earlier, due to the inversion symmetry of a homonuclear diatomic molecule, DA through a single NIR will not provide any asymmetry in the angular distribution of the ions. So how might such an observed asymmetry arise? We show below that the asymmetry can be explained in terms of the interference of two dissociating quantum paths if the electron attachment leads to the coherent formation of two NIRS of opposite parity. This takes place by attachment of the s-wave (\(l = 0\)) and the p-wave (\(l = 1\)) of a free electron coherently to form NIRS of \(\Sigma_u\) and \(\Sigma_g\) symmetry, respectively. These two NIRS eventually dissociate to the same limit through their respective potential energy curves, defining two interfering quantum paths, as shown in Fig. 3. For these two coherently formed NIRS, the angular distribution of the fragment ions is given by

\[
f(\theta) = \sigma_{DA} + 3\sigma_{DA} \cos^2 \theta + 2 \cos \delta \cos \theta \sqrt{\sigma_{DA}} \sigma_{DA} \|
\]

where \(\sigma_{DA}\) and \(\sigma_{DA} \) are the DA cross sections for each of the channels contributing and \(\sqrt{\sigma_{DA}}\) and \(\sqrt{\sigma_{DA}}\) indicate the corresponding probability amplitudes of the contributions of the two states to the DA cross section, \(\theta\) is the angle of ejection of the H\(^-\) anion with respect to the incoming electron beam, and \(\delta\) is the relative phase between the two channels at the dissociation limit.

The extent of the asymmetry, which is seen as the contrast in the interference pattern, depends on the relative phase between two paths and the relative amplitudes of the wavepackets traversing the two paths. Phase differences between these two paths will then occur as the two NIRS evolve along the two distinct potential energy curves. The relative amplitudes of the two paths depend on the capture cross section associated with each NIR and its ‘survival probability’ against autodetachment, which is given by

\[
p_c = \exp \left( - \int_{R_k}^{R_B} \Gamma(R) \frac{dR}{\hbar\nu(R)} \right) = \exp \left( - \int_{R_k}^{R_B} \frac{dt}{\tau(R)} \right)
\]

where \(\Gamma(R)\) is the width of the anion potential energy curve, \(\nu(R)\) is the speed of separation of the dissociating atoms, \(R_k\) is the internuclear separation where the electron capture takes place and \(R_B\) is the effective inter-nuclear separation beyond which the molecular anion is considered to be dissociated. \(\tau(R)\) is the corresponding lifetime of the NIR.

Effects due to survival probability are more prominent in the case of heavier isotopes, as they have longer dissociation times. As the survival probability of the NIR varies exponentially with the time for dissociation, the likelihood of a given resonance surviving against autodetachment in D\(_2\) is considerably smaller compared to that in H\(_2\). This has long been recognized as the basis for the strong isotope effect in DA in molecular hydrogen and its isotopomers\(^{16}\). If one of the two coherent NIRS decays much faster compared to the other then the contrast of the interference between the two will be weakened. This situation is akin to putting an absorbing material in one arm of an optical interferometer, thereby reducing the contrast of the interference fringes.

From the momentum images we have derived the forward-backward asymmetry, \(\eta = (I_B - I_F)/(I_B + I_F)\), at selected energies across the 14 eV resonance, where \(I_B\) and \(I_F\) are the forward and backward signal strengths with respect to the incoming electron beam, determined as the respective angle-integrated counts in the forward (+ve \(P_3\)) and backward (−ve \(P_3\)) directions with respect to the horizontal axis (90°). The values of \(\eta\) are presented in Table 1. However, it can be seen that, in the case of H\(_2\), the asymmetry is negative at all energies due to the larger backward intensity. The asymmetry in D\(_2\), although small, is in the opposite direction at 14 eV and changes direction as we change the electron energy.

To model the observed results quantitatively it is necessary to have detailed information on the potential energy curves and lifetimes of the NIRS that are involved. There have been several electron scattering studies on H\(_2\) and D\(_2\) which have provided a wealth of information on their NIRS, as reviewed by Schulz\(^{19}\). However, very little information is available for the 14 eV process as compared to that for the 4 eV and 10 eV processes. Transmission as well as scattering experiments had indicated the presence of a \(\Sigma^+_g\) NIR in the 11 eV to 13.5 eV range\(^{20,21}\). The same NIR was identified in the electron scattering experiments at 14 eV with a width of...
Figure 2 | Velocity slice images of H\(^-\) from H\(_2\) and D\(^-\) from D\(_2\) at different electron energies. a–g, Velocity slices have been converted to momentum images. The electron beam direction is from bottom to top of the figure. Note that whereas the intensity distribution is symmetric for H\(^-\) at 4.5 eV, it is asymmetric at higher energies and that the asymmetry is substantially lower for D\(^-\).

Figure 3 | Schematic of the DA process at 14 eV in H\(_2\) and D\(_2\). The dashed long arrows indicate electron attachment to form the coherent states \(2\Sigma^+\) and \(2\Sigma^+_g\). For electron energies above 13.92 eV these states dissociate to form the negative ion (H\(^-\)/D\(^-\)) and the neutral atom (H/D) in the \(n=2\) state. As the wavepackets of these states travel towards the dissociation limits they continuously decay through electron ejection, as shown by the broad faint arrows marked ‘a’. For H\(_2\), the wavepackets reach the dissociation limit with more or less similar amplitudes, resulting in strong interference and the consequent asymmetry in the momentum distribution, as indicated by the velocity slice image. However, for D\(_2\) one of the wavepackets has lost most of its amplitude and hence there is a relatively small interference effect, yielding the almost symmetric momentum distribution observed in the image. Please see the text for more details as well as the simulation results given in Fig. 4.

The energy shift for the \(2\Sigma^+_u\) state in both the simulations. For the results in Fig. 4a,c we used a curve that follows the B' \(\Sigma_u^+\) state of the neutral, but with an appropriate energy shift\(^25\). In a similar way, plots in Fig. 4b,d were obtained by using the potential energy curve that follows the C' \(\Pi_u\) curve of neutral H\(_1\) (ref. 25) with a downshift in energy. As expected the pattern strongly depends on the potential energy curves as well as lifetimes of the resonant states involved. The overall forward–backward asymmetry is seen to decrease with electron energy. These oscillations are ‘faster’ if the two dissociating paths are considerably different, as in the case of Fig. 4a,c, and ‘slower’ when the two paths

90 meV (ref. 21). Subsequent DA measurements concluded that this \(\Sigma^+_u\) NIR is the main contributor to the 14 eV DA process\(^22\) and this has been the accepted wisdom until now\(^26,23\). Extensive R-matrix calculations\(^24\) give several NIRS of \(\Sigma_u\) and \(\Sigma_g\) symmetry above 12 eV. However, the overlap of these curves with the Franck–Condon region is below the energy range of interest here, even after taking their widths into account.

One can estimate the amount of forward–backward asymmetry for a given electron energy if one knows the potential energy curves for the resonances involved and their widths as a function of inter-nuclear separations. Such an estimate of the asymmetry for two sets of potential energy curves as a function of the lifetime of the ungerade state and electron energy is shown in Fig. 4. The asymmetry shows an oscillatory pattern. Please refer the Methods for the details of the model. We have used an average lifetime of 8 fs for the \(2\Sigma_u^+\) state based on the reported width of 90 meV at 14 eV (ref. 21) and the potential energy curve given by Sharp\(^20\) for the \(2\Sigma_u^+\) state in both the simulations. For the \(2\Sigma_u^+\) state, we have used two different curves. For the results in Fig. 4a,c we used a curve that follows the B' \(\Sigma_u^+\) state of the neutral, but with an appropriate energy shift\(^25\). In a similar way, plots in Fig. 4b,d were obtained by using the potential energy curve that follows the C' \(\Pi_u\) curve of neutral H\(_1\) (ref. 25) with a downshift in energy. As expected the pattern strongly depends on the potential energy curves as well as lifetimes of the resonant states involved. The overall forward–backward asymmetry is seen to decrease with electron energy. These oscillations are ‘faster’ if the two dissociating paths are considerably different, as in the case of Fig. 4a,c, and ‘slower’ when the two paths...
A comparison of the present results with the observed symmetry breaking following single-photon absorption in H₂ (ref. 26) may be appropriate. The photoabsorption in H₂ at 33 eV leads to the creation of an autoionizing state which then decays by electron ejection to two ionic states of opposite parity, both of which dissociate to the same H⁺ + H limit. The corresponding ejected electron angular momentum is a superposition of odd and even parity, leading to an asymmetry in the angular distribution with respect to the molecular axis. The major difference in the present case is that the attachment of a single electron necessarily leads to the creation of a coherent superposition of two autodetaching resonances of opposite parity, which on surviving autodetachment show interference in dissociation.

To conclude, coherent excitation of two resonant states of a homonuclear diatomic molecule by electron attachment results in symmetry breaking in dissociative attachment. Such coherence stems from various partial waves of the attaching electron, and the resulting quantum paths interfere as they lead to the same dissociation limits. This scenario may be observed in particular in electron attachment, but may also occur more generally in particle scattering as it allows more than one value of angular momentum transfer with comparable strength, unlike photoabsorption. It is also interesting to note that the preference of H⁺ ejection in one direction as against the ejection of an excited H atom demonstrates the localization of charge and energy acquired by the molecule in electron attachment. This also provides direct evidence of the role of electron-electron correlations in terms of energy and charge segregation in the dissociation process. The asymmetry in the fragmentation of D₂ is weaker, indicating the reduced strength of the interference in D₂. This is due to the slower dissociation of the resonant states of D₂, resulting in relatively larger depletion of the amplitude of one of the dissociating channels through autodetachment. The situation is similar to two interferometers with

are fairly close, as in the case of Fig. 4b,d. The differences between H₂ and D₂ are clearly visible if one compares panel a with panel c and panel b with panel d. For a given lifetime of the \( ^2\Sigma^+ \) state, the amplitude of the oscillation is smaller in D₂ compared to that in H₂. This is consistent with the qualitative description given earlier and as depicted in Fig. 3. We also note that Fig. 4b,d shows qualitative agreement with the experimental data (Table 1) and the degree of asymmetry does not change substantially in this case over a range of electron energies as in the case of the measured data for H₂. The directional change of the asymmetry with electron energy in the case of D₂ is also seen. From these qualitative agreements we predict that the two potential energy curves have similar shapes so that the phase difference between the two paths does not change drastically with energy. We wish to point out that curves used in this case are almost empirically chosen and only more accurate potential energy curves along with their lifetimes will allow us to fully understand the details of the coherent dynamics of this DA process.

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different arm lengths and with an absorbing medium of differing thickness in the two arms. These results highlight the need, as well as the challenges, in developing full quantum dynamical calculations for DA to even the simplest system, such as H\textsubscript{2}. Lastly, we wish to point out that the formation of coherent states we observe in the DA process may be far more general than has been recognized until now, and the signatures of such coherent effects may exist in electron scattering from molecules in general. Moreover, the coherent excitations of anion states also hint at more possibilities of electron-induced chemical control.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

E.K. and N.J.M. planned the research. E.K. built the experiment with help from N.J.M. and carried out the measurements. V.S.P. carried out the simulations and E.K. and V.S.P. interpreted the results. E.K. and V.S.P. prepared the manuscript.

Additional information

Supplementary information is available in the online version of this paper. Reprints and permissions information is available online at http://www.nature.com/reprints. Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Correspondence and requests for materials should be addressed to E.K.

Competing financial interests

The authors declare no competing financial interests.
Methods

Experimental apparatus. We carried out the measurements using the velocity slice imaging technique\(^1\). In this, a pulsed (200 ns pulse duration) electron beam is allowed to interact with an effusive molecular beam produced from a long capillary tube. A low magnetic field (50 G) is used to collimate the electron beam. The product anions are extracted into a velocity-mapping time-of-flight spectrometer mounted at right angles to the electron beam direction using a pulsed electric field after a delay of 200 ns with respect to the electron pulse. The ions are detected using a two-dimensional position-sensitive detector including a Z-stack of three 75-mm-diameter microchannel plates and a phosphor screen\(^2\). The image on the phosphor screen is recorded using a charge-coupled device (CCD) camera. Velocity slice imaging can be carried out by pulsing the detector and the phosphor bias corresponding to the arrival of the central slice of the Newton sphere of the relevant ion at the detector—however, due to the low signal levels, data were taken with relatively wide slices.

Model for the forward–backward asymmetry. With \(\tau_g\) and \(\tau_u\) as the average lifetimes of the gerade and ungerade resonant states involved in DA, \(t_g\) and \(t_u\) as the dissociation times for the parent anion along the respective potential energy curves for electron attachment with a specified energy, and assuming equal capture cross section for both the resonances, the forward–backward asymmetry, \(\eta\), can be obtained as

\[
\eta = \frac{\sqrt{3} \exp\left[-(t_g/2\tau_g + t_u/2\tau_u)\right]}{\exp[-(t_g/\tau_g)] + \exp[-(t_u/\tau_u)]} \cos\delta
\]

where \(\delta\) is the relative phase between the two paths of dissociation for the anion resonant states given by

\[
\delta = \frac{1}{R_c} \int_{R_c}^\infty \left[\sqrt{2\mu(E - V_g(R))} - \sqrt{2\mu(E - V_u(R))}\right] \, dR + \frac{\pi}{2}
\]

Here \(R_c\) is the inter-nuclear separation corresponding to the electron capture, \(\mu\) reduced mass of the dissociating system, \(E\) is the electron energy and \(V(R)\) is the potential energy corresponding to the given resonant state with respect to the \(v = 0\) level of the neutral ground state.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.