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Molecular physics: Breaking up is hard to do

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MOLECULAR PHYSICS

Asymmetric separation

The presence of quantum effects at the atomic and molecular level holds promise for controlling chemical reactions. Experiments now reveal the role of quantum interference in breaking a fundamental symmetry in the dissociation of homonuclear diatomic molecules by resonant electron impact.

D. S. Slaughter and T. N. Rescigno

Molecular dissociation is one of the most fundamental chemical reactions, playing a role in many natural and technological processes. Despite its pervasiveness, its physics is by no means simple, and in many cases it defies a classical explanation and can only be accurately described using quantum mechanics. Now, writing in *Nature Physics* [1], E. Krishnakumar and co-workers have found an asymmetry in dissociative electron attachment to hydrogen molecules— an apparent breaking of the inversion symmetry due to quantum interference effects.

Striking examples of coherent symmetry breaking in molecular systems have previously been found in photoionization of homonuclear diatomic molecules [2-4]. In those cases, photoexcitation to one or more highly excited electronic states is followed by autoionization [2,3], or delayed photoionization [4], and, ultimately, dissociation via multiple pathways. The quantum amplitudes of each channel sum coherently when the final state kinetic energies are identical, leading to interference. Broken inversion symmetry can then be measured in the momentum distributions of the atomic fragments and the emitted electron. In contrast, the symmetry breaking reported by Krishnakumar *et al.* is initiated entirely by electrons: the electron attachment creates a coherent superposition of two resonances with opposite parity.

In their experiments, electron impact seems to create two excited states of the H_2^- anion, which can either decay by autodetachment or dissociate to an excited hydrogen atom, $\text{H}(n=2)$ and the bound hydride ion, $\text{H}^-(1s^2)$. If the two resonance states were well separated in energy, then dissociation at a fixed electron energy would proceed through one or the other state and no asymmetry in the products would be detected. However, if the two resonance states are of opposite parity and lie closer in energy than their respective decay widths, then the initial electron-molecule resonance is a superposition of the two electronically excited anion states and their probability amplitudes must be added coherently. The measured momentum of the anion fragment reveals asymmetry, created by interference between the two anion resonances. In the case of H_2 , the H^- asymmetry was found to decrease with increasing incident electron energy, whereas running the experiment on D_2 molecules showed an asymmetry increased for D^- over the same electron attachment energy range. This seems to be a direct result of coherent electron attachment forming two resonant states of the excited molecule, followed by dissociation along two pathways to the same final state (see Figure 1).

The resonance states involved are undoubtedly doubly excited (or Feshbach) resonances, namely states in which an electron attaches to an excited state of the neutral target. Such states typically have very small widths at equilibrium geometry, but there is theoretical evidence that such resonances can become sufficiently broad to overlap at smaller inter-nuclear separations within

the Frank-Condon region. Indeed, resonance states predicted previously [5] seem to be candidates that can support the observed data.

Despite recent advances in electronic structure theory and computational techniques [6, 7] the energies and lifetimes of the anion resonances are challenging to calculate. From the onset of an electron attachment reaction, electron-electron correlations can strongly couple the electronic and nuclear degrees of freedom, leading to a clear and immediate breakdown of the Born–Oppenheimer approximation. As the molecular anion dissociates, the autodetachment lifetimes of the resonance states also change, until the transient electron-molecule system becomes electronically bound when its potential energy crosses below that of the neutral excited state. Accurate modelling of such highly non-equilibrium systems, even for the simplest diatomic molecule, requires a coherent sum of all the possible decay and dissociation channels, and therefore accurate knowledge of the resonance potential energy curves and their autodetachment lifetimes. In lieu of such a detailed theoretical approach, Krishnakumar *et al.* have demonstrated the validity of their physical description using approximate potential energy curves derived from neutral excited states of H₂, presenting simulated breakdown of inversion symmetry consistent with their experimental observations.

In this fundamental example of inversion-symmetry breaking by electron impact on a homonuclear diatomic molecule, Krishnakumar and coworkers presented mechanisms, due to quantum interference effects, that may be generally applicable to many resonant electron-driven reactions. Such highly differential particle spectroscopy experiments, when combined with new theoretical developments in accurately describing the motion of correlated electrons, highly excited electronic states and autoionization, could reveal further surprises in resonant electron–molecule interactions.

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References

1. E. Krishnakumar *et al.* *Nature Phys.* xxx (2017)
2. Lafosse *et al.* *J. Phys B*, **36** 4683 (2003).
3. Martin *et al.* *Science* **315** 629-633 (2007).
4. Sansone *et al.* *Nature* **465** 763-766 (2010).
5. Stibbe, D. T. & Tennyson, J. *J. Phys. B* **31** 815 (1998)
6. M. A. Fennimore *et al.*, *Phys. Chem. Chem. Phys.*, **19**, 17233-17241 (2017)
7. D. S. Slaughter *et al.* *J. Phys. B*, **49** 222001 (2016); see also references therein

Figure 1 | Schematic representation of resonant electron attachment (green vertical arrow) producing coherent dissociating wavepackets on two electronic states (red and blue curves), with opposite parity, of the transient anion H_2^- . The lower black curve is the ground electronic state of H_2 and the upper black curve is the neutral excited electronic state participating in the autodetachment decay channel, where a non-radiative transition may occur from either anion state (blue or red curve) to the excited neutral state by emitting an electron. Competing with autodetachment, dissociation occurs on both anion states. The energies of the anion states overlap for the molecular geometry during electron attachment, so their coherent contribution to dissociation leads to interference and broken inversion symmetry.