

Importance of Nonresonant Scattering in Low-Energy Dissociative Electron Attachment to Molecular Hydrogen

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(Received 23 March 2006; published 7 July 2006)

A central premise of nearly all theories of dissociative electron attachment is that this process is resonance driven. Neglect of nonresonant scattering, although appropriate for electron-molecule systems with narrow (long-lived) resonances, is problematic for the e -H₂ system, which has one of the broadest known resonances. Using the nonadiabatic phase-matrix method we have found that at energies from threshold to 6 eV contributions from nonresonant scattering to cross sections to dissociative attachment to H₂ in its ground vibrational and electronic state exceed 60%. Comparison of theoretical and experimental cross sections argue strongly for further efforts to resolve the considerable remaining discrepancies over this most elementary rearrangement process.

DOI: 10.1103/PhysRevLett.97.013201

PACS numbers: 34.80.Ht

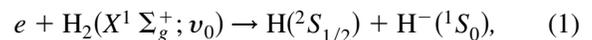
Dissociative electron attachment (DEA), in which an incident electron causes a molecule to dissociate and attaches to one of the resulting atomic fragments, compels attention as the simplest rearrangement collision in molecular physics. The energy transfer that enables DEA is essentially nonadiabatic and in most systems is resonance driven. These features make DEA essentially a many-body process. As the molecule dissociates, quite different physical mechanisms may come into play—e.g., long-range coupling of asymptotically degenerate electronic states, and, for polyatomic targets, coupling involving rotational and vibrational motion of a molecular fragment. DEA plays a major role in a diverse array of physical processes, including combustion, the physics of planetary atmospheres, diagnostics of magnetic fusion devices [1], and models of gas discharges and low-temperature plasmas [2–4]. DEA is also of urgent environmental importance, e.g., in understanding the formation of the “ozone hole” above Antarctica [5]. For these reasons DEA to a host of molecules continues to engage intense experimental and theoretical attention [6–12].

With few exceptions, the development of theories of DEA [13,14] forms a succession of increasingly powerful, sophisticated approaches based on the assumption that DEA is entirely resonance driven (for recent reviews, see [15,16]). Thus the most recent and accurate measurement of cross sections for DEA to H₂($X^1\Sigma_g^+$; 0) describes this process as occurring “via the 4 eV resonance” and characterizes cross sections by a “resonance width” which the experiments seek to determine. The predominant theoretical approaches to DEA—the quasiclassical single-pole R -matrix method [17–19] and the nonlocal resonance model (NLRM) [7]—invoke this assumption.

The assumption that coupling of the scattering electron dynamics and the nuclear motion occurs *solely* through a resonant state is certainly viable for DEA to molecules via reasonably long-lived (narrow) resonances. This assump-

tion is problematic, however, for DEA of H₂ near 4 eV. The resonantlike enhancement in cross sections near this energy is exceptionally broad, corresponding to a lifetime comparable to the time for nonresonant autodetachment of the electron.

This feature of the e -H₂ system raises the question of whether treatments and conceptualizations based on the formal assumption of purely resonant scattering (e.g., via a discrete state embedded in the continuum [20]) are appropriate for low-energy DEA to H₂. Assessing this question is very difficult in most theories, usually because a resonance model is embedded in the theories themselves [7,18,21]. We have investigated this question using a theory that allows quite easily for inclusion or omission of nonresonant scattering: the nonadiabatic phase-matrix (NADP) method [22–24]. Here we report on low-energy DEA to H₂,



where v_0 denotes the initial vibrational state of H₂ in its ground $X^1\Sigma_g^+$ electronic state.

NADP theory fully takes into account nonadiabatic effects that are vital to DEA. Nonadiabatic effects, which allow energy transfer between the electronic and nuclear degrees of freedom of the $(N+1)$ -electron system that cannot occur in a Born-Oppenheimer (“adiabatic”) treatment, enable the transfer of sufficient energy to dissociate the molecule [e.g., to dissociate $e + \text{H}_2(X^1\Sigma_g^+; v_0)$ to $\text{H}(^2S_{1/2}) + \text{H}^-(^1S_0)$ requires at least 3.723 eV]. The NADP method includes nonadiabatic effects through the construction, from fixed-nuclei (FN) R matrices calculated on a hypersurface S_0 , of a *vibronic* R matrix $\mathbb{R}(E; S_0)$, where E is the total system energy. For DEA to H₂, this hypersurface is defined by two coordinates: a value r_0 of the radial position of the scattering electron (we take $r_0 = 10.0a_0$), and a value R_0 of the internuclear separation (we

take $R_0 = 2.50a_0$). The vibronic T matrix produces cross sections for DEA and for vibrational excitation (VE) [24].

To obtain this T matrix, we propagate the vibronic R matrix from the hypersurface $S_0 = (r_0, R_0)$ to asymptotic values of r (for VE) and R (for DEA). In this “outer region” the potential for VE is a simple analytic function of r that arises from the permanent-quadrupole and induced-dipole interactions of the scattering electron and the molecule. The potential for DEA is that of the dissociating atom and anion.

The vibronic R matrix $\mathbb{R}(E; S_0)$ contains resonant and nonresonant contributions; nonresonant contributions can easily be omitted if desired. This facility obtains because $\mathbb{R}(E; S_0)$ is constructed from resonant (“foreground”) and nonresonant (“background”) *phase matrices* [22]. These phase matrices are *fixed-nuclei* quantities calculated at S_0 from FN R matrices, which incorporate electron dynamics in the inner (near-target) region, and so-called Bloch eigenfunctions, which appear in conventional R matrix theory (cf. Ref. [21]). Bloch eigenfunctions are eigenfunctions of the sum of a nuclear Hamiltonian and the Bloch operator [25]. The nuclear Hamiltonian is the sum of a kinetic-energy operator for nuclear vibration and the R -dependent potential energy of the “precursor resonance” [22], which we calculate on a grid of internuclear separations as described in Ref. [23]. The Bloch operator discretizes the spectrum by imposing Neumann boundary conditions at S_0 .

We write each FN phase matrix as the sum of a resonant FN phase matrix and a nonresonant FN phase matrix. Analysis of resonant FN phase matrices yields R -dependent quantities that, together with the Bloch eigenfunctions and eigenvalues, we use to construct the *resonant* vibronic phase matrix $\Phi^{\text{res}}(E; S_0)$ [23,24]. The nonresonant FN phase matrices may be used to calculate a *nonresonant* vibronic phase matrix $\Phi^{\text{nonres}}(E; S_0)$ via the energy-modified adiabatic (EMA) approximation [22–24]. The sum of the resonant and nonresonant phase matrices yields the final vibronic R matrix

$$\mathbb{R}(E; S_0) = \mathbf{k}^{-1/2} \tan[\Phi^{\text{res}}(E; S_0) + \Phi^{\text{nonres}}(E; S_0)] \mathbf{k}^{-1/2}, \quad (2)$$

where \mathbf{k} is a diagonal matrix of channel wave numbers. *Resonance-only cross sections*, in which nonresonant scattering is neglected, are generated by simply omitting $\Phi^{\text{nonres}}(E; S_0)$ in this equation.

A detailed description of NADP theory, its key equations, and our implementation for VE of H_2 appear in Refs. [23,26]. Derivations and implementation for DEA will appear in Ref. [27]. We note that our calculation of the FN R matrices do not require direct solution of the $(N + 1)$ -electron problem in the inner region; the NADP implementation requires only single-electron calculations [23]. For the R -dependent potential energy $V_0^-(R)$ in the external region $R > R_0$ we use the accurate H_2^- potential

from multireference configuration-interaction calculations by Senekowitsch *et al.* [28], the same potential used by Horáček *et al.* [7], whose cross sections we compare to below. At energies below 6 eV, the largest energy we consider, DEA is dominated overwhelmingly by scattering in the $^2\Sigma_u$ electron-molecule symmetry [7,29], the only symmetry we include.

Figure 1 shows cross sections for DEA to $\text{H}_2(X^1\Sigma_g^+; 0)$ with and without nonresonant scattering. We find that nonresonant scattering increases the cross section by an average of 60% over the whole energy range from threshold to 6.0 eV. The effect is not monotonic; with increasing energy it varies slowly from about 60% just above threshold to a minimum of 37% at 5.22 eV and a maximum of 85% at 5.8 eV. Comparable increases occur when these results are Boltzmann averaged and energy convoluted for comparison to experiment [see Fig. 2].

The most recent and accurate measurement of near-threshold DEA cross sections to $\text{H}_2(X^1\Sigma_g^+; 0)$ are those of Drexel *et al.* [30]. These authors performed experiments in two different high-resolution crossed-beam apparatuses: a hemispherical electron monochromator at a gas temperature of 300 K with a resolution of 100 meV [full width at half maximum (FWHM)], and a trochoidal monochromator at 400 K with FWHM of 200 meV. They normalized their measured relative $\text{H}^-(^1S_0)$ ion yield to the absolute values at 14 eV measured by Rapp *et al.* [31]. Drexel *et al.* emphasize that because of the nature of the experiments, direct comparison of theoretical DEA cross sections like those in Fig. 1 to measured values may lead to qualitatively misleading conclusions. Meaningful comparison requires two additional steps. First, theoretical DEA cross sections for a range of initial *rovibrational* states (v_0, j_0) must be

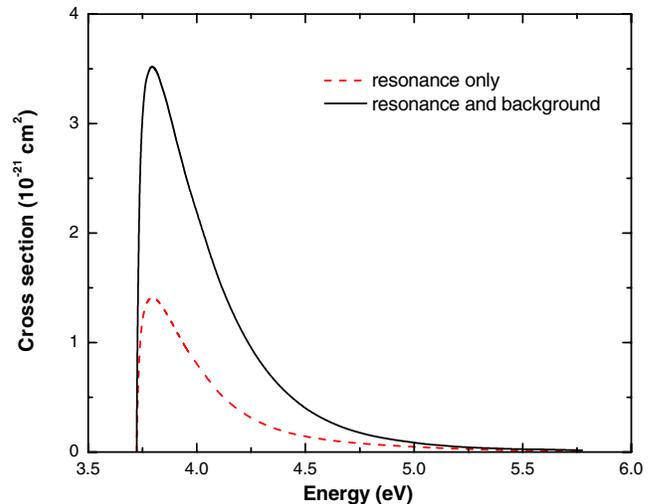


FIG. 1 (color online). Cross sections for dissociative attachment of $\text{H}_2(X^1\Sigma_g^+; 0)$ as a function of the kinetic energy of the incident electron measured with respect to the ground vibrational state of H_2 : resonance scattering only (dashed); resonance and background scattering (solid).

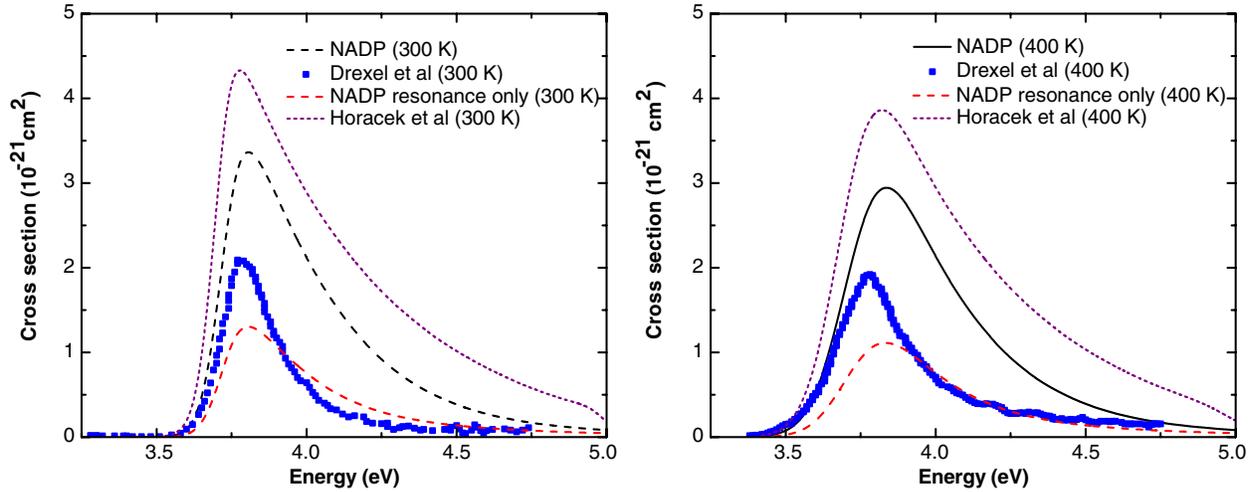


FIG. 2 (color online). DEA cross sections for $\text{H}_2(X^1 \Sigma_g^+; 0)$ at $T = 300$ K (left panel) and $T = 400$ K (right panel). Curves: NADP results with (solid) and without (dashed) nonresonant contributions, and NLRM results of Horáček *et al.* [7] (dotted). Theoretical data have been averaged over a Boltzmann distribution of rotational states and convolved over the experimental energy resolution function as discussed in the text. Points: experimental data of Drexel *et al.* [30].

averaged over the Boltzmann population probability at the stated gas temperature. Second, the results of this averaging must be convolved with the apparatus function to take into account the experimental distribution of electron energies. Comparing Figs. 1 and 2 shows that these steps broaden the leading edge of the DEA cross section.

NADP calculations produce a *vibronic* T matrix (within the fixed-nuclear-orientation approximation [32]) that cannot be used directly to calculate the *rovibrational* cross sections required for Boltzmann averaging. We have therefore extended the rotational frame transformation theory [33], which is widely used in studies of elastic and vibrationally inelastic scattering [34], to rearrangement collisions [35].

Figure 2 compares NADP cross sections (with and without nonresonant scattering) to the NLRM results of Horáček *et al.* [7] and to data from the two experiments in [30]. All theoretical cross sections have been Boltzmann averaged and energy convolved. At $T = 300$ K the theoretical FWHM is 363.2 meV, and the NADP cross section exceeds the experimental data by as much as 89% at 4.29 eV. At $T = 400$ K the theoretical FWHM is 436.5 meV and the NADP cross section exceeds the data by as much as 71% (at 4.13 eV). Peak energies and cross sections are compared in Table I.

When our averaged DEA cross sections are conormalized to the data of [30] at the peak, their onset behavior below the peak is virtually identical to that of the data;

TABLE I. Peak energies and values of cross sections for DEA to $\text{H}_2(X^1 \Sigma_g^+; v_0 = 0)$. The constant E_0 is a fitting parameter in the exponential fitting function (3). The quantity χ^2 is the merit function for the fit. The threshold for this process is $\epsilon^{\text{th}} = 3.723$ eV.

	E_{peak} (eV)	σ_{peak} (10^{-21} cm 2)	E_0 (eV)	χ^2
NADP	3.794	3.528	0.382	0.95
NADP resonance only	3.794	1.414	0.350	0.14
Horáček <i>et al.</i> [7]	3.729	4.758		
Boltzmann averaged and energy convoluted (300 K)				
NADP	3.796	3.377		
NADP resonance only	3.796	1.309		
Horáček <i>et al.</i> [7]	3.771	4.338		
Drexel <i>et al.</i> [30]	3.77	2.09		
Schulz and Asundi [36]	3.75	1.75		
Boltzmann averaged and energy convoluted (400 K)				
NADP	3.844	2.951		
NADP resonance only	3.844	1.113		
Horáček <i>et al.</i> [7]	3.819	3.867		
Drexel <i>et al.</i> [30]	3.78	1.92		

above the peak, however, the conormalized theoretical cross sections are appreciably broader than the experimental values, whether or not nonresonant scattering is taken into account. This disparity over the width of the DEA cross section is more acute in comparison to the averaged NLRM cross sections of [7], since the NLRM cross sections are broader than ours. (Comparisons to earlier theoretical results, appear in Ref. [30]; widths predicted by these earlier calculations are also appreciably larger than those in Fig. 2.)

We have fitted the theoretical cross sections discussed in this Letter to the form [37]

$$\sigma^{\text{DEA}}(E) = \sigma_{\text{peak}} \exp\left[-\frac{E - \epsilon^{\text{th}}}{E_0}\right]. \quad (3)$$

The resulting values of the fitting parameter E_0 , which appear in Table I, are appreciably smaller than the value $E_0 = 0.45$ eV quoted in [37], which was obtained by a fit to the NLRM results of Atems and Wadehra [38].

In conclusion, we have examined the widely held view of DEA as exclusively resonance driven for DEA to $\text{H}_2(X^1\Sigma_g^+; 0)$ at energies below 6 eV: we have found that contributions from nonresonant scattering exceed 60%. NADP theory facilitates inclusion or omission of nonresonant scattering via its use of phase matrices. Although based on single-electron fixed-nuclei quantities, NADP theory incorporates nonadiabatic effects in the vibronic R matrix at the hypersurface between the internal (near-target) and external regions. Comparison of theoretical and experimental DEA cross sections argue strongly for further efforts to resolve the considerable remaining discrepancies over this most elementary rearrangement process.

We acknowledge useful conversations with Dr. Ilya Fabrikant, Dr. Gregory A. Parker, and Dr. R. K. Nesbet. We thank Professor Fabrikant and Professor Jiří Horáček for sending us cross sections, and Dr. Wolfgang Sailer for sending us the data of Drexel *et al.* [30] and helping us with their analysis. This work was supported by the National Science Foundation under Grant No. PHY-0354858.

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