Nuclear Instruments and Methods in Physics Research B 279 (2012) 71–75

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Resonant inelastic collisions of electrons with diatomic molecules

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ARTICLE INFO

Article history:
Received 21 July 2011
Received in revised form 27 September 2011
Available online 25 November 2011

Keywords:
Electron–molecule collisions
Vibrational excitation
Dissociative electron attachment
Nonlocal resonance model

ABSTRACT

In this contribution we give a review of applications of the nonlocal resonance theory which has been successfully used for treating the nuclear dynamics of low-energy electron collisions with diatomic molecules over several decades. We give examples and brief explanations of various structures observed in the cross sections of vibrational excitation and dissociative electron attachment to diatomic molecules such as threshold peaks, boomerang oscillations below the dissociative attachment threshold, or outer-well resonances.

1. Introduction

Theoretical description of the dynamics of low-energy resonant electron–molecule collisions involving nuclear dynamics proceeds usually in two steps. First, potential energy surfaces of the molecule and molecular anion are determined and fixed-nuclei electron scattering calculations revealing resonant character of these processes are performed using one of a few available packages of codes based e.g. on the *R*-matrix method [1], complex Kohn variational method [2], or Schwinger multichannel method [3,4]. The second step involves calculation of the nuclear dynamics on a certain level of approximation. The most common is the local complex potential approximation introduced by Bardsley [5] and the nonlocal resonance model reviewed by Domcke [6], but there are also other approaches such as *R*-matrix method of Fabrikant et al. [7,8], which is equivalent to the nonlocal resonance model, or of Schneider et al. [9]. Comparison of some approximations used for the nuclear dynamics and their validity for different systems was discussed recently using simple two-dimensional model of electron–molecule collisions [10] and it was shown that the nonlocal resonance theory can give correct results for systems where other approximations such as the local complex potential approximation fail [11].

Here we provide a brief summary of available nonlocal resonance models for diatomic molecules which where used to calculate resonant contributions to the cross sections of processes such as

$$e^- + AB(v_i) \;\rightarrow\; e^- + AB(v_f), \tag{1}$$

which includes both elastic scattering and inelastic vibrational excitation, and the competing process of dissociative electron attachment

$$e^- + AB(v_i) \;\rightarrow\; A + B^-. \tag{2}$$

The same calculation can, of course, provide also the full information about the reverse process of associative detachment. We also give a survey of various structures appearing in the cross section and discuss their origin due to the nuclear motion in the molecular anion potential.

2. Overview of nonlocal resonance models

The first full nonlocal resonance model (NRM) of a real system was constructed for electron collisions with N_2 by Berman et al. [12] and the results were found in very good agreement with experimental data of Wong et al. [12] and of Ehrhardt and Willmann [13]. Since then, this system has served as a benchmark for various approaches applied to resonant electron–molecule collisions. Other nonlocal resonance models followed for hydrogen halides and hydrogen molecule (discussed in more details below) and also for a few other systems such as halogen molecules F_2 and Cl_2 to which the Fano–Feshbach-*R*-matrix method was applied [14,15] which constructs the model functions of the NRM directly from *ab initio* fixed-nuclei *R*-matrix calculations [16].

2.1. Hydrogen halides

The importance of electron collisions with hydrogen halides and their deuterated analogs lies in richness of structures which were observed in the vibrational excitation (VE) and dissociative attachment (DA) cross sections. Threshold peaks and Wigner cusps,

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doi:10.1016/j.nimb.2011.10.057

oscillatory structures, or outer-well resonances are ubiquitous in these cross sections as we illustrate in Fig. 1 where the integral VE and DA cross sections are plotted for HCl (upper panel) and HBr (lower panel). These phenomena demanded for explanation and thus motivated the theoretical work on the resonant electron–molecule collisions. One of the first papers on the full nonlocal theory of electron–molecule collisions by [17] was devoted to hydrogen halides. In this paper, the authors constructed the first, rather qualitative nonlocal resonance models for HF, HBr and HCl and showed that the nonlocal theory is general enough to explain different types of threshold phenomena.

The most studied hydrogen–halide systems has been $e^- + HCl$ and $e^- + HBr$ for which several nonlocal resonance models based on the *ab initio* fixed-nuclei scattering data and quantum-chemical calculations of lowest potential-energy curves of neutral molecule and molecular anion have been constructed. The first models by Domcke and Mündel [20] for HCl and by Horáček and Domcke [21] for HBr were later improved by including a variable threshold exponent to take into account the internuclear dependence of the molecular dipole moment [22] which turned out to be important to get the proper threshold behavior of the VE cross section where a sharp onset peak appears, and also by including new HCl^- [23] and HBr^- [19] potential-energy functions for large internuclear distances which were more attractive resulting in more pronounced oscillatory structures below the DA threshold and even in very narrow, outer-well resonances as we can see in Fig. 1.

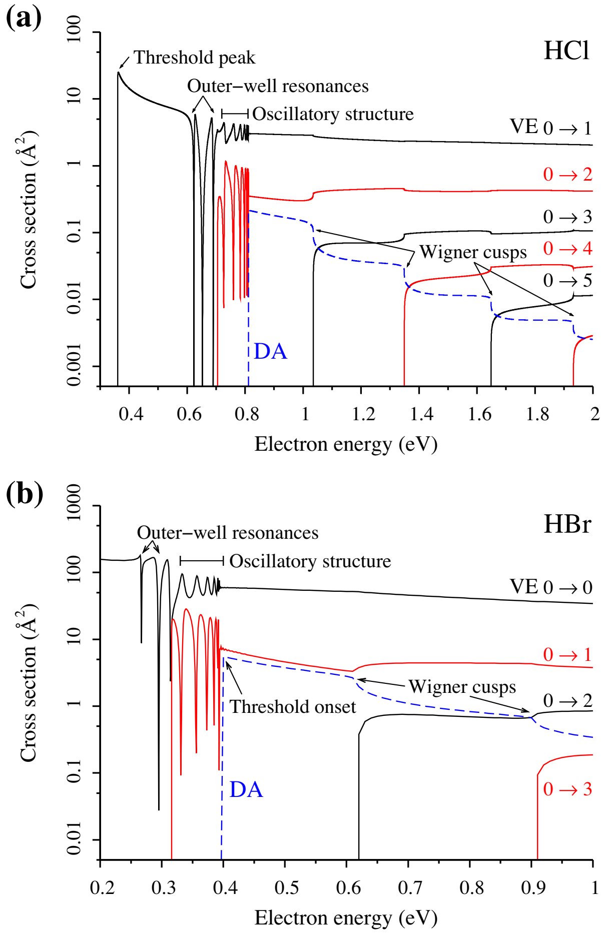

Fig. 1. The calculated integral cross section of vibrational excitation and dissociative electron attachment for the molecule HCl up to 2 eV (upper panel) and HBr up to 1 eV (lower panel). The results of the most recent nonlocal resonance models for HCl [18] and HBr [19] are shown.

The most recent nonlocal resonance model for HCl was build on new fixed-nuclei scattering data [18]. The motivation for this new model was disagreement of the experimental DA cross section measured recently by Fedor et al. [24] with the calculated one by the model of Čížek et al. [23]. The DA cross section from the ground vibrational state of HCl obtained by this last model was about twice less than in the previous calculations in agreement with the experiment. The illustrative comparison of these models with experimental data of Schafer and Allan [25] and of Allan et al. [26] is shown in Fig. 2. The rate constants for dissociative attachment and associative detachment for HCl and HBr based on the NRM cross sections were published in [27].

The system $e^- + HF$ is an example of a system where the molecule possesses a supercritical dipole moment. The construction of NRM is therefore more complicated [28,29] than for other systems but the agreement found between theory and experiment was again quite good, see [29]. In Fig. 3, lower panel, we plotted examples of the cross sections from the ground vibrational state discussed in more detail in the next section.

The molecule HI is the only hydrogen halide for which parameters of the nonlocal resonance model were fitted to the experimen-

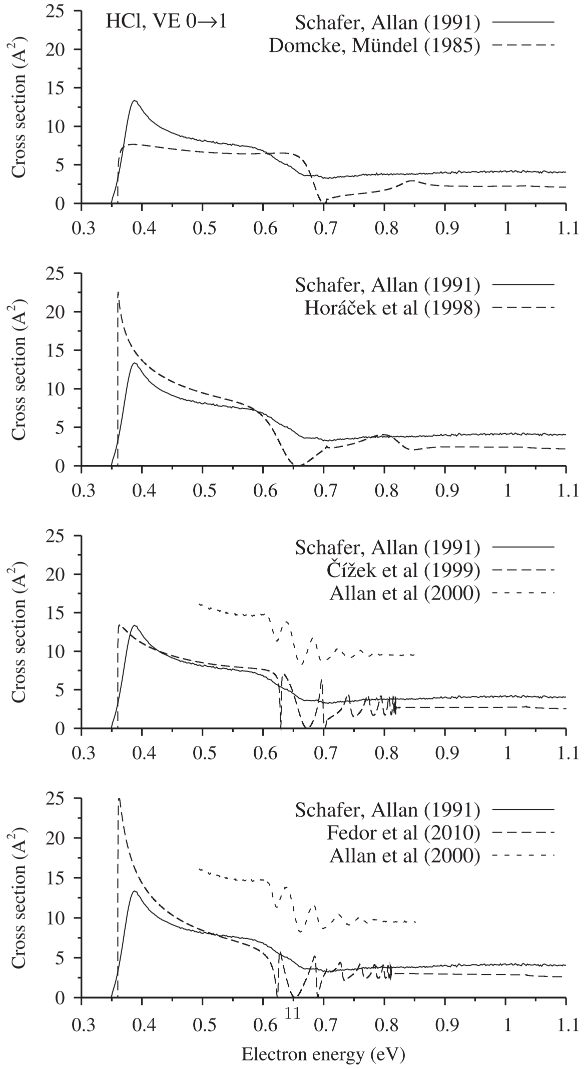

Fig. 2. The comparison of integral cross section of vibrational excitation from the ground state of the molecule HCl to the first excited state as calculated using different nonlocal resonance models (see text for references) with experimental results of Schafer and Allan [25] (scaled to the threshold peak of the NRM of Čížek et al. [23]) and of Allan et al. [26].

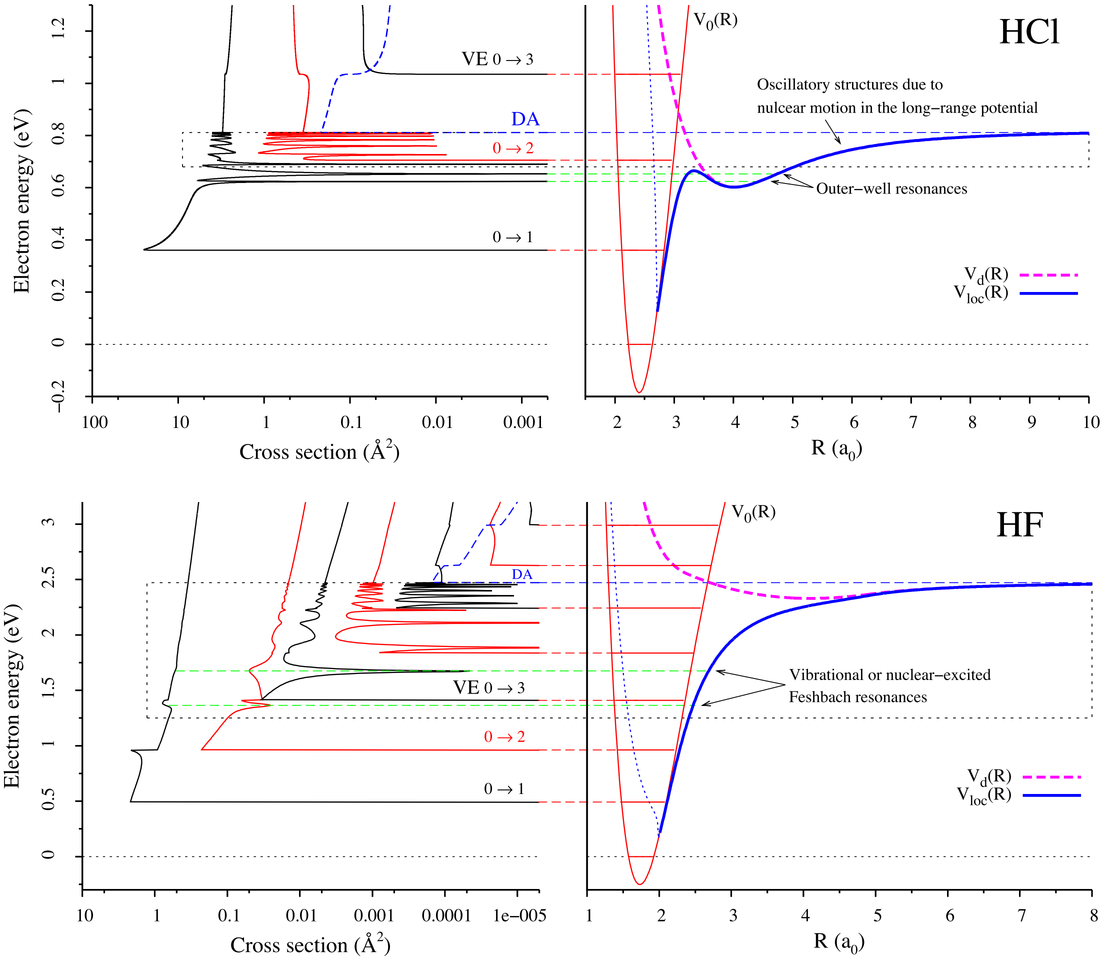

Fig. 3. The calculated integral cross section of vibrational excitation and dissociative attachment for HCl and HF are plotted next to the potential energy curves to highlight the origin of various structures in the cross sections. The results of the most recent nonlocal resonance models for HCl [18] and HF [19] are shown.

tal cross section because *ab initio* electron scattering calculations had not been available. Horáček et al. [30] built the NRM for HI by fitting the DA cross section of [31] in the energy range 0–200 meV and used this model to calculate the DA cross section for higher energies and the VE cross sections which were found in rather good agreement with the experiment. An unexpectedly large resonant contribution to elastic electron scattering on DI at energies below the DA threshold was calculated and published later by Horáček et al. [32]. A series of sharp peaks of very large amplitudes of order of hundreds and even thousands of Å^2 appears in the elastic cross section for the molecule in its ground rovibrational state. These structures can be interpreted as outer-well resonances due to the nuclear motion of the DI$^-$ (see Fig. 3 for examples of such resonances in the case of HCl).

2.2. Hydrogen molecule

The low-energy collisions of electrons with the hydrogen molecules are of importance in several fields of physics, especially in astrophysics, and therefore this system has been the most studied one both experimentally and theoretically by many different approaches including the nonlocal theory (see e.g. [33,34] and references therein). Although it is the simplest system (at least considering the number of electrons), an accurate calculation of the dynamics of the collision and interpretation of the structures found in the cross sections have proved to be quite difficult.

At energies up to 6 eV, only $H_2^-\ {}^2\Sigma_u^+$ shape resonance contributes significantly to the VE and DA cross sections. There are two NRM based on *ab initio* calculations for this system. The first model based on the *ab initio* data of [35] was constructed by Mündel et al. [36] who also predicted the oscillatory structure in the VE cross sections for higher transitions which was confirmed experimentally by Allan [37]. The second NRM [38] improved the first model by taking into account a new data for the H_2^- potential energy curve calculated by [39]. The origin of the oscillatory structure for H_2 was a puzzle since Gertitchke and Domcke [40] proposed that the oscillations in the VE cross sections are of a different origin than the well-known *boomerang* oscillations observed in the $e^- + N_2$ system. Although alternative, but unnecessarily complicated and sometimes inaccurate explanations of the oscillatory structures were proposed in the literature, see for example [41–43], a simple interpretation was provided in [34] where it was shown that these structures are actually pure boomerang oscillations (see also [44] for more arguments supporting this explanation).

3. Structures in the cross sections

We have illustrated the richness of the structures in the VE and DA cross sections in Fig. 1. In Fig. 3 we show several VE cross section for HCl and HF next to the potential energy curves which are used in the NRM calculations. First, we can notice a clear relation between position of the threshold peaks and Wigner cusps and the energies of bound vibrational states of the molecule as other VE channels open. Several possible mechanisms of the enhancement of the cross sections at the thresholds were initially proposed which included the effects of virtual states, *s*-wave bound states, or resonances (see [6] for details and references). But it was soon recognized that the difference between these mechanisms is vague since all of them are included in a unified way within the nonlocal theory, which provides particularly suitable theoretical framework to describe and explain all these threshold phenomena and to distinguish among them is neither necessary nor sometimes possible. A detailed discussion of analysis of potential-energy curves involved in electron–molecule collisions near threshold as singularities of the fixed-nuclei electron–molecule scattering matrix was given in [6].

Other remarkable structures observed in the VE cross sections, as we can see in Fig. 3, are oscillations below the DA threshold which are sometimes known as boomerang oscillations according to the boomerang model of Birtwistle and Herzenberg [45] which was the first model explaining similar oscillations in the $e^- + N_2$ system. These oscillations result from interference between two processes, a direct electron detachment and a time-delayed electron detachment due to the boomerang-like motion of the nuclei to larger internuclear distances, see Fig. 3, left panels, where the long-range potentials of negative molecular ion are shown. Main features of the oscillatory structures are following. The absolute magnitude of the oscillations near the DA threshold is almost the same in the VE cross sections from a given initial vibrational state to different final states (note that in Fig. 3 the VE cross sections are plotted in the logarithmic scale), the oscillations are narrowing with increasing electron energy towards the DA threshold, and finally the amplitude inversion of the oscillations can be observed from one final vibrational state to the next one. All these properties can be easily explained within boomerang model, see [34] for details. If similar structures appear in the VE cross sections in the vicinity of the vibrational bound states of the neutral molecule (like for HF right below the $0 \rightarrow 3$ and $0 \rightarrow 4$ VE thresholds, see Fig. 3, lower panel) they are usually called vibrational or nuclear-excited Feshbach resonances [46] but it should be noted here that there is often no clear borderline between these two notions and both structures appear due to nuclear motion of the negative molecular ion.

Finally, there are very narrow structures in the VE cross sections called the outer-well resonances which often appear as irregularities in the otherwise rather regular oscillatory structure discussed above. We can see clear examples of such resonances in the VE cross section for HCl in Fig. 3, upper panel, where their relation to resonant states in the potential well of the negative molecular ion outside the autodetachment region at smaller internuclear distances, where the electron can escape and the neutral molecule can be formed, is apparent. For some systems as $e^- + H_2$ the potential well appears only for higher rotational molecular states and play an important role in creation of long-lived states of the molecular anion which were observed experimentally and explained within the nonlocal theory by [47] for H_2^- and D_2^-.

4. Conclusions

Nuclear dynamics of low-energy electron collisions with diatomic molecules is well described and understood within the nonlocal resonance theory. The structures observed in the vibrational excitation and dissociative attachment cross sections are of two types. *Threshold effects* appear at the openings of new channels and *structures due to the nuclear motion*, which include boomerang oscillations, outer-well resonances, and vibrational Feshbach resonances, differ often only slightly and it is sometimes difficult to distinguish among them.

Although the latter structures can be explained qualitatively even within the local complex potential approximation, application of the nonlocal resonance theory is often necessary to get quantitative agreement with experiments.

Acknowledgements

Support from the Czech Science Foundation (GAČR) by Grant No. 208/10/1281 and by Záměr MSM0021620860 of the Ministry of Education, Youth and Sports of the Czech Republic is gratefully acknowledged.

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