

Giant structures in low-energy electron–deuterium-iodide elastic scattering cross section

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(Received 2 October 2006; revised manuscript received 1 December 2006; published 26 February 2007)

Calculations of the resonance part of the cross section of elastic electron scattering with DI molecule at energies below the dissociative attachment threshold based on the use of the nonlocal resonance model of Horáček, Nakamura and Domcke [Z. Phys. D **42**, 181 (1997)] reveal a series of sharp peaks of giant amplitudes of several thousands of Å^2 . These structures are interpreted as demonstrations of outer well resonances in the negative molecular ion state potential and should be observable experimentally provided the energy resolution of the beam is in the range of few meV.

DOI: [10.1103/PhysRevA.75.022719](https://doi.org/10.1103/PhysRevA.75.022719)

PACS number(s): 34.80.Bm

Oscillatory structures in elastic as well as inelastic cross sections in electron-molecule collisions at electron energies below the threshold for the dissociative attachment (DA) are now well known. They were first predicted for vibrational excitation $v=0 \rightarrow 3,4$ of H_2 by Mündel, Berman, and Domcke [1] and their existence was confirmed experimentally soon after by Allan [2], see also [3,4]. Structures of this type have been subsequently found in hydrogen halides HF, HCl, and HBr, see, e.g., [5–10]. Closely related and much more studied are the boomerang oscillations in the scattering of electrons with molecular nitrogen [11,12], although in this case the DA process does not exist. As an example of structures right below the DA threshold, in Fig. 1, the resonance contribution to the integral elastic electron scattering cross sections for the ground rovibrational state of the HCl and HBr calculated with the nonlocal resonance model are shown together with the experimental data [7,8]. In this figure the calculated resonance contribution to the elastic cross section which is isotropic in the scattering angle (*s*-wave resonance scattering) is compared with the measured vibrationally elastic cross section recorded at 90° . The agreement between the calculated and measured cross sections confirms the high accuracy and reliability of the nonlocal resonance model. In cases mentioned above the amplitude of the oscillations was rather small and the oscillations represented mostly a kind of fringe pattern on the otherwise smooth cross sections.

The magnitude of the oscillations was discussed in [4] in relation with the vibrational excitation of molecular hydrogen where the oscillations are very regular. In [4] it was argued that the magnitude of the oscillations near the threshold is proportional to the magnitude of the DA process at the threshold. Similar behavior can be observed for the other molecules such as hydrogen halides. The dissociative attachment process opens at the energy 2.47 eV for HF, 0.81 eV for HCl, and 0.39 eV for HBr and the lower is the threshold energy, the greater is the peak value of the DA cross section and the magnitude of the oscillations in the VE cross section. In the case of HI the process of dissociative attachment is exothermic and the cross section diverges at $E \rightarrow 0$. Therefore no oscillations were observed in electron-HI scattering. For the deuterium iodide, however, the ground rovibrational state moves to energies below the DA threshold and the dissociative attachment opens at a positive energy of 35.5 ± 1 meV [13]. Since it is known that the magnitude of the DA cross section for DI attains the threshold value of

hundreds of Å^2 , see [14] and Fig. 2, and since the potential energy curve of DI^- is long range and sufficiently attractive to support several quasibound states right below the DA threshold, see Fig. 3, one may expect oscillatory structure of huge amplitude of the order of thousands of Å^2 in the elastic electron DI cross sections at very low energies. The purpose of this paper is to predict the existence of these huge structures and to show that they may be observable in modern experiments with high electron energy beam resolutions (see below).

The calculations discussed here are based on the use of the nonlocal resonance model (NRM) [15] which is the most advanced description of the resonant electron-molecule collisions. The nonlocal resonance model is defined by the three functions $V_0(R)$, $V_d(R)$, and $V_{de}(R)$. The target potential-energy function $V_0(R)$ can directly be obtained from *ab initio* calculations. For both HCl and HBr the model parameters could be determined from *ab initio* fixed-nuclei electron-scattering data by a simple fitting procedure [5]. Since this information is not available for the *e*-HI system the model parameters were adjusted such that the high-resolution low-energy attachment data of Klar *et al.* [16] were reproduced. The potential function $V_d(R)$ for large R has been recovered from accurate *ab initio* calculations [17] of the HI^- potential-energy function. A full description of the model is given in [14]. It should be noted that the nonlocal resonance model functions for DI are the same as for HI since the model is based on the fixed-nuclei electronic calculations. The only model parameter which is changed for DI is the reduced mass of the molecule.

For better understanding of the dynamics of the *e*-DI system, in Fig. 3, the potentials $V_0(R)$ and $V_d(R)$ used in the nonlocal resonance model together with the real part of the local approximation to negative molecular ion potential energy are plotted. When the electron is captured into the resonant state DI^- the wave function describing the nuclear motion is localized in the potential well of $V_0(R)$ (green, long dashed curve). As this state evolves, at certain energies it tunnels through the inner barrier around $R=4$ a.u. into the outer well of the negative molecular ion potential (black, solid curve) where it can live for a long time depending on the width of the inner barrier. These long-lived states of molecular ion correspond to sharp resonant structures in the elastic cross section. We will return to a mathematical description of these structures later.

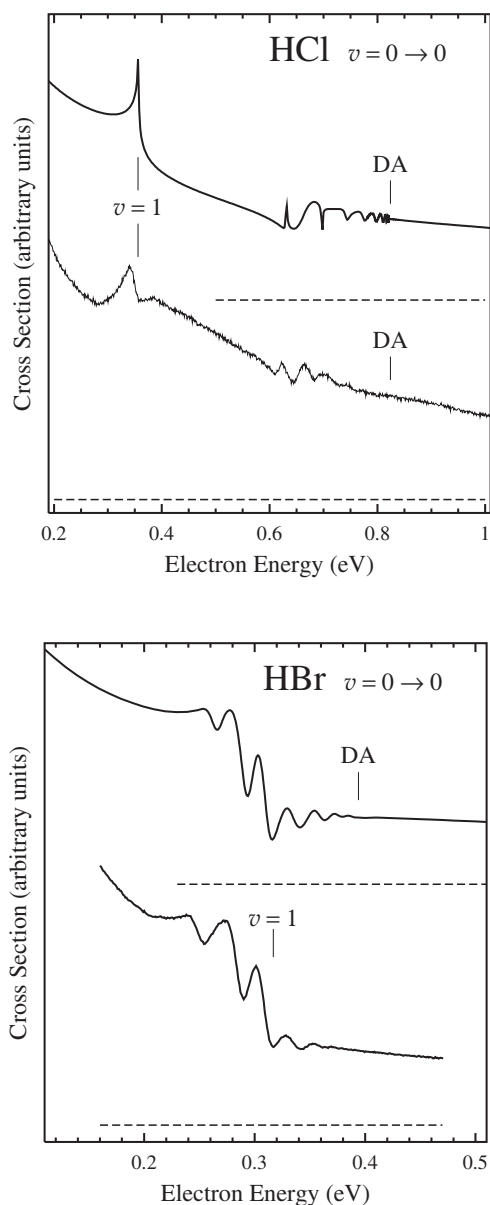


FIG. 1. Calculated resonance contribution to the integral elastic electron scattering cross section for the ground rovibrational state of the HCl, top panel, and HBr, bottom panel. Upper parts: nonlocal resonance model (NRM) calculations, lower part: measured vibrationally elastic cross section recorded at 90° [7,8].

In Fig. 4 the calculated resonance contribution to the elastic-scattering cross section is presented for the DI molecule in its rotationally and vibrationally ground state $v=0$ and $J=0$, i.e., for zero temperature of the gas. As we expected, the cross section exhibits very sharp peaks with the magnitude of several thousands of \AA^2 corresponding to the ten long-lived states of DI^- . Energies of these states are approximately equal to the energies of the bound states of the potential V_L depicted in Fig. 3 by solid lines. Seven bound states of DI^- , which lie below the ground rovibrational state of DI (dotted lines), do not affect the elastic cross section. For the full elastic cross section one has to add the nonresonance part which is assumed to be large but a smooth function of the electron energy and which does not change sig-

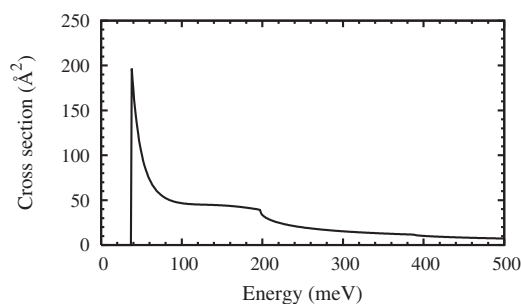


FIG. 2. DA cross section for DI molecule in its ground rovibrational state [14].

nificantly positions of the peaks. The same argument holds also for the HBr and HCl elastic cross sections shown in Fig. 1.

In a real experiment two effects must be taken into account: finite energy resolution of the electron beam described by the full width at the half maximum (FWHM), and non-zero temperature T of the target gas. Let us first discuss the role of the energy resolution of the beam. In Fig. 5 we plot the calculated resonance contributions to the elastic-scattering cross sections for the gas temperature 1 K (results are virtually identical for all lower temperatures) and the FWHM of the electron energy distribution 1, 2, and 3 meV. Huge oscillations are present in the cross sections even at FWHM=3 meV. At FWHM=1 meV the magnitude of the oscillations reaches the value of 1000\AA^2 , at 3 meV the magnitude is several hundreds of \AA^2 .

Figure 6 corresponds to the gas at the temperature of liquid nitrogen, $T \approx 80 \text{ K}$. At this temperature higher rotational states are occupied. For these states the positions of the peaks are shifted to lower energies. After averaging over the Maxwellian distribution of the initial states the resulting structures in the cross section are highly irregular but again the oscillations are clearly discernible even though their magnitude is reduced (400\AA^2 at FWHM=1 meV).

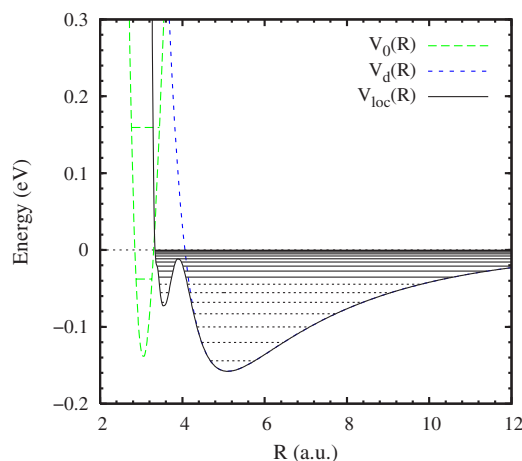


FIG. 3. (Color online) Potentials of the DI system: Green (long dashed) line, potential of the ground electronic state of DI with first two vibrational states; blue (short dashed) line, the discrete state potential V_d ; black solid line, the real part V_L of local negative ion state potential. The horizontal solid lines indicate the bound states in this real potential V_L .

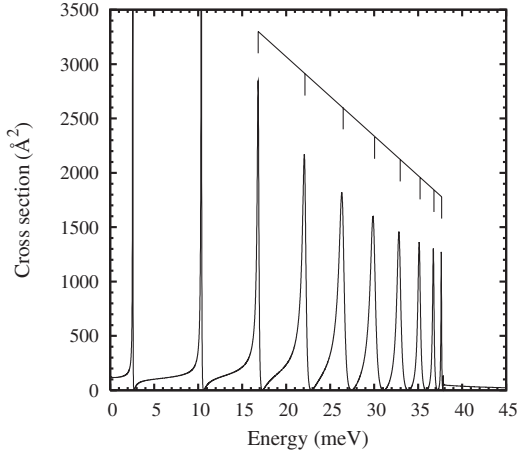


FIG. 4. Calculated resonance contribution to the elastic-scattering cross section for the ground states $v=0$ and $J=0$ of the DI. Positions of several bound states of the potential V_L , see Fig. 3, are also shown.

Finally, in Fig. 7 we plot the elastic resonance contribution for the room temperature $T=300$ K. Even at the room temperature the oscillations are clearly seen with a huge amplitude of about 200 \AA^2 for FWHM=1 meV and of about 100 \AA^2 for 2 meV. Since it is possible in modern experiments, see, e.g., [18], to obtain an electron energy resolution ranging from 0.75 to 1.5 meV at very low energies down to 10 meV these structures should be observable even at the room temperature.

Let us now return to the mathematical description of the sharp peaks observed in the cross section in Fig. 4. These structures can be interpreted in terms of the nonlocal resonance model as follows. The resonance contribution to the vibrational excitation cross section (including elastic one for $f=i$) is given as [15]

$$\sigma(E, v_i \rightarrow v_f) = \frac{4\pi^3}{k_i^2} |\langle v_f | V_{dE_f} | \psi_{dE}^{(+)} \rangle|^2. \quad (1)$$

Here V_{dE_i} is the coupling between the discrete and the continuum states and

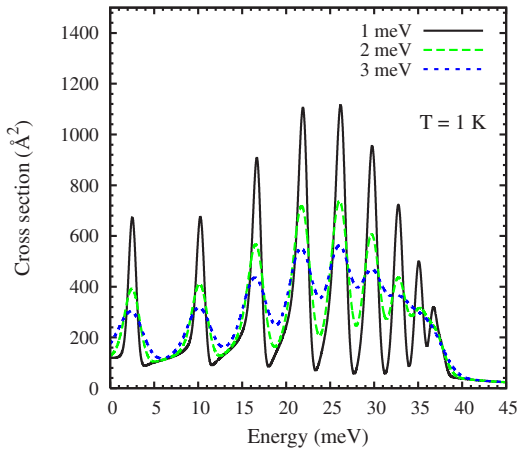


FIG. 5. (Color online) Calculated resonance contribution to the elastic-scattering cross section for temperature of DI, $T=1$ K, and electron beams with FWHM 1, 2, and 3 meV.

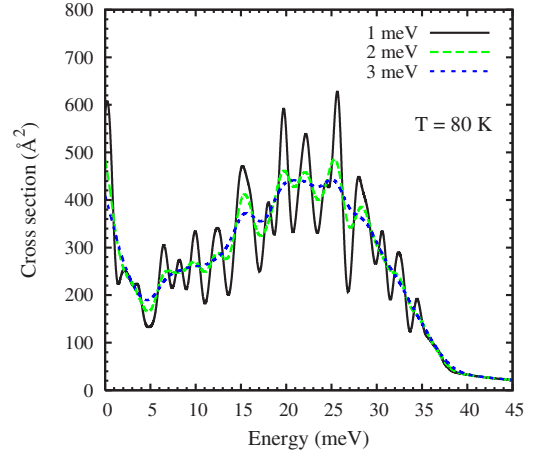


FIG. 6. (Color online) The same as Fig. 5 but for the temperature of liquid nitrogen 80 K.

$$|\psi_{dE}^{(+)}\rangle = G_0^{(+)} V_{dE_i} |v_i\rangle + G_0^{(+)} (V_d + F) |\psi_{dE}^{(+)}\rangle, \quad (2)$$

where

$$F(E; R, R') = \Delta(E; R, R') - \frac{i}{2} \Gamma(E; R, R') \quad (3)$$

is the nonlocal potential governing the resonance dynamics [15], v_i and v_f are the initial and final vibrational wave functions of the molecule, $G_0^{(+)}$ is the free-particle scattering Green's function, and V_d is the potential of the discrete state.

We now define a real local potential V_L as a real part of the local complex approximation [15] to $V_d + F$ which merges with the discrete state potential at large and intermediate internuclear distances; see Fig. 3. We subtract this potential from the discrete state potential V_d :

$$|\psi_{dE}^{(+)}\rangle = G_0^{(+)} V_{dE_i} |v_i\rangle + G_0^{(+)} [V_L + (V_d - V_L + F)] |\psi_{dE}^{(+)}\rangle \quad (4)$$

and denote $V = V_d - V_L + F$. Let us next define Green function, $G_L^{(+)}(E)$, corresponding to the potential V_L , by

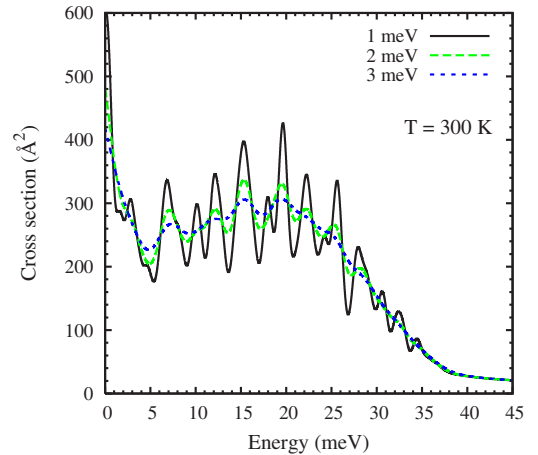


FIG. 7. (Color online) The same as Fig. 5 but for the room temperature of DI, $T=300$ K.

$$G_L^{(+)}(E) = (1 - G_0^{(+)}V_L)^{-1}G_0^{(+)} \quad (5)$$

Then Eq. (4) can be rewritten as

$$|\psi_{dE}^{(+)}\rangle = G_L^{(+)}V_{dE_i}|v_i\rangle + G_L^{(+)}V|\psi_{dE}^{(+)}\rangle \quad (6)$$

The spectral decomposition of the Green function $G_L^{(+)}$ has the form

$$G^{(+)} = \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{E - E_n}, \quad (7)$$

where $|\psi_n\rangle$ are bound and continuous solutions of

$$\left(-\frac{\hbar^2}{2\mu}\Delta + V_L(R)\right)|\psi_n\rangle = E_n|\psi_n\rangle \quad (8)$$

with appropriate boundary conditions.

In the process of vibrational excitation below the DA channel the total energy E is negative. If the energy E is close to one of the eigenvalues E_j we can write the Green function in the form

$$G_L^{(+)} = \frac{|\psi_j\rangle\langle\psi_j|}{E - E_j} + R(E), \quad \text{for } E \approx E_j, \quad (9)$$

where the remainder R is a smooth function of energy. Neglecting this smooth part we can express the VE cross sections as (the role of R is discussed in [19])

$$\sigma \approx \frac{4\pi^3}{k_i^2} \frac{|\langle v_f|V_{dE_f}|\psi_j\rangle\langle\psi_j|V_{dE_i}|v_i\rangle|^2}{|E - E_j - \langle\psi_j|\text{Re } V + i \text{Im } V|\psi_j\rangle|^2} \quad (10)$$

where $\text{Re } V$ and $\text{Im } V$ represent the real and the imaginary part of the potential V , respectively. For states ψ_j which are localized at the outer edge of the interaction region the level shift $\langle\psi_j|\text{Re } V|\psi_j\rangle$ and the width $\langle\psi_j|\text{Im } V|\psi_j\rangle$ will be small and the cross section will peak around each E_j . This is

clearly demonstrated in Fig. 4 where the vertical bars indicate the position of E_j below the DA threshold. The peaks of the cross sections coincide almost exactly with the E_j values. Because of possibility of autoionization the E_j do not correspond to true bound states but rather narrow resonances. At an electron energy close to E_j the electrons live long in the resonance complex what is reflected in the cross section.

Concluding, we can state that the existence of narrow and extremely high peaks in the elastic scattering of a low-energy electron with DI molecule is predicted. The origin of the peaks can be attributed to the existence of quasibound states of the $D+I^-$ system located at large internuclear distances. Though narrow the peaks should be observable in an experiment even at room temperature provided the energy resolution of the electron beam is in the range of few meV. Such experiments are now available [18]. Since the position of the peaks is given by a very precise quantum chemistry calculation they might be used for calibration purposes if the molecules are cooled down. It is expected that structures of this nature might exist in many molecules for which the process of DA opens at a small positive energy and if the molecular ion potential is sufficiently attractive to support long-lived quasibound states. In all applications of the nonlocal resonance model carried out so far the resonance lifetime of the transient negative ion was so short that the probability to change the rotational state of the molecule (rotational excitation) has been neglected to a good approximation. In a future work we plan to address this issue together with the detailed study of the interference of the resonance contribution with the direct one.

Support from the Czech Academy of Sciences by Grant No. GAAV IAA400400501 and by Výzkumný záměr MSM0021620835 “Fyzika molekulárních, makromolekulárních a biologických systémů” of MŠMT is greatly acknowledged.

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