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Isotope effects in vibrational excitation and dissociative electron attachment of DCl and DBr

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Abstract. The results of calculations of vibrational excitation and dissociative electron attachment cross-sections of DCl and DBr are reported. The calculations are based on the nonlocal resonance model for electron-HCl/HBr scattering. The cross-sections for many initial rovibrational target states were calculated both for the hydrogenated and the deuterated compounds. The calculations reveal an unexpected result: the vibrational excitation cross-section of the deuterated molecule may in some cases be (significantly) larger than that of the hydrogenated compound. This effect is observed when the target molecule is initially excited to a vibrational state the energy of which is close to the threshold of dissociative attachment. Rotational excitation of the target molecule plays a similar role. Isotope effects in dissociative electron attachment are also discussed.

PACS. 38.40.Ht Dissociation and dissociative attachment by electron impact – 34.80.Gs Molecular excitation and ionization by electron impact

1 Introduction

Electron-molecule collision processes play an essential role in many areas of physics, astrophysics, chemistry, biology and technology [1]. Among them, three inelastic processes are particularly important: vibrational excitation (VE) by electron impact

$$e + \mathrm{AB}(J,v) \to e + \mathrm{AB}(J,v'), \tag{1}$$

dissociative electron attachment (DA)

$$e + \mathrm{AB}(J,v) \to \mathrm{A} + \mathrm{B}^- \tag{2}$$

and associative electron detachment (AD)

$$\mathrm{A} + \mathrm{B}^- \to e + \mathrm{AB}(J,v'). \tag{3}$$

All three processes can be described by the so-called nonlocal resonance model [2]. This model is based on the assumption that a temporary molecular negative-ion state (resonance) is formed and that this resonance accounts for the coupling of the electronic scattering dynamics with the nuclear motion. The resonance is represented by a square-integrable discrete state $|\varphi_d\rangle$ which interacts with a continuum of scattering states $|\varphi_\varepsilon\rangle$ via coupling matrix elements $V_{d\varepsilon}$. $|\varphi_d\rangle$ and $|\varphi_\varepsilon\rangle$ are assumed to be diabatic states, that is, their wave functions vary smoothly with the internuclear distance R.

The second essential ingredient of the nonlocal resonance model especially for hydrogen halides is the explicit consideration of threshold effects induced by the long-range dipole potential. The dipole-induced nonanalyticities of the S matrix and related quantities at threshold enter through the threshold expansion of the energy-dependent width function

$$\Gamma(\varepsilon) = 2\pi|V_{d\varepsilon}|^2 \tag{4}$$

and the associated level shift $\Delta(\varepsilon)$ [2]. Since this model was described in detail in the literature, we refer the reader to the original papers (see e.g. [3–6]). Here, we concentrate on the discussion of the obtained results.

In the past several years we have carried out an extensive study of VE, DA and AD cross-sections for hydrogen halides based on generalised and improved nonlocal resonance models [3–9]. These calculations have provided detailed cross-sections and electron spectra for many initial and final rovibrational states of the target molecules in very good agreement with available experimental data. In the present paper, we report calculated DA and VE cross-sections for DCl and DBr. The purpose of this contribution is twofold: (i) to present new data for the DA and VE processes in DCl and DBr and (ii) to study the isotope effect, i.e., the changes of the DA and VE cross-sections when the hydrogen atom is replaced by the heavier deuterium atom.

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2 Isotope effects

Isotope effects in low-energy electron-molecule collisions are well-known. Of particular importance is the substitution of deuterium or tritium for hydrogen, because the effects are more pronounced as a result of the greater change of the reduced mass. Let us mention as an extreme example the process of DA in molecular hydrogen

$$e + \mathrm{H}_2 \rightarrow \mathrm{H} + \mathrm{H}^-. \tag{5}$$

According to the measurements of Schulz and Assundi [10, 11], the peak cross-section is smaller by a factor of about ten in HD that in H_2. In D_2, the DA cross-section is about 200 times smaller than in H_2. Such isotope effects are expected also in DA of hydrogen halides (HF, HCl, HBr and HI), but are less pronounced, see e.g. [3,4]. The DA cross-sections of the heavier molecules are always smaller than those of the lighter ones. This is the so-called normal isotope effect.

The isotope effect can be explained as follows (see, e.g., [12]): DA is a resonance process, that is, a short-lived negative molecular ion state is formed in the process of the electron-molecule collision. During the lifetime of the resonance state, the molecular constituents move on a repulsive potential curve (see the solid line in Fig. 1). If the nuclei succeeded to separate beyond a critical distance R_c, the channel of autodetachment becomes closed and the process of DA is completed. Obviously, the magnitude of the DA cross-section depends on the time the nuclei need to travel to the critical point R_c. For a given collision energy, the speed of the deuterated molecules is smaller than that of the hydrogenated ones, and consequently a smaller fraction of the anions succeeds in passing the critical distance R_c. This leads to a reduction of the DA cross-section in the deuterated molecules. To the knowledge of the authors, the only exception of this rule was reported by Sharp and Dowell [13] for deuterated methane.

Isotope effects also have been observed in VE, but have gained much less attention. To the best of our knowledge, only two papers have addressed this problem. Chang and Wong [14] based on the use of frame-transformation theory and later Atems and Wadehra [15] using local complex potential approach proposed an approximate theory of the isotope effect in VE. According to this theory, the ratio of the VE cross-sections for DX and HX molecules, where X = F, Cl, Br, is independent of the energy and depends only on the initial and final vibrational states v_i and v_f as well as on the reduced mass μ

$$\frac{\sigma(\mathrm{DX})}{\sigma(\mathrm{HX})} \approx \left(\frac{\mu_{\mathrm{DX}}}{\mu_{\mathrm{HX}}}\right)^{-\frac{1}{2}|v_i - v_f|}. \tag{6}$$

This theory was applied also to molecular hydrogen and predicts, for example, that the $0 \rightarrow 1$ VE cross-section of D_2 is smaller by a factor of $1/\sqrt{2} \sim 0.71$ than that of H_2. In a real experiment carried out by Chang and Wong [14] at a nonzero temperature T, two isotope effects are in fact seen: one, due to the change of the reduced mass, is that all cross-sections behave as indicated in equation (6), the other enters via the changes in rotational-state populations (different nuclear spin statistics and rotational constants). If this is taken into account the theory agrees very well with the experiment. For example the predicted ratio for the $v = 0 \rightarrow 1, \Delta J = 0$ transition at 4.0 eV is 0.56 whereas the experimental value is 0.55 [14]. For the transition $v = 0 \rightarrow 1, J = 0 \rightarrow 2$ the theory yields the value 0.71 and the experiment 0.72. According to [15] the scaling law, equation (6), is accurate with the error less than 35%.

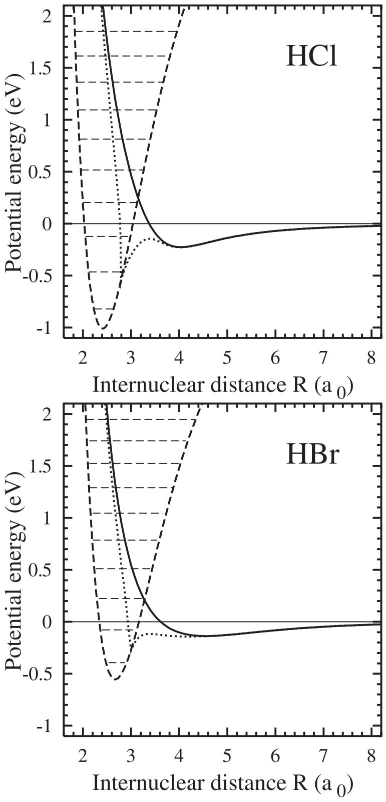

Fig. 1. Potential-energy curves for HCl and HBr molecules and their negative ions; long dashes: potential energy of the neutral molecule; short dashes: potential energy of the molecular transient anion; solid line: discrete-state potential. Horizontal lines indicate positions of vibrational levels of the neutral molecules.

3 Results

3.1 Vibrational excitation

The calculated VE cross-sections of DCl from the vibrational ground state are shown in Figure 2. Threshold peaks are clearly seen in the channels $v = 0 \rightarrow 1, 2$ and 3. For comparison, we show in Figure 3 also cross-sections for HCl molecules (for a detailed discussion of VE of HCl we refer the reader to [3]). Our calculations show that the theory of Chang and Wong [14] and Atems and Wadehra [15] is in this case qualitatively correct (calculation of the ratio of the VE $0 \rightarrow 1$ cross-sections for DCl and HCl molecules

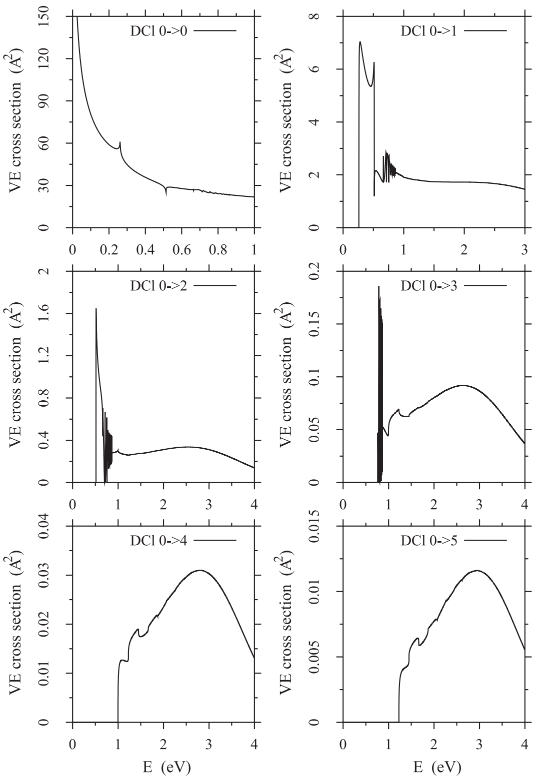

Fig. 2. Vibrational excitation of DCl: $v = 0 \to 0, ..., 5$. Integral cross-sections are given in Å^2.

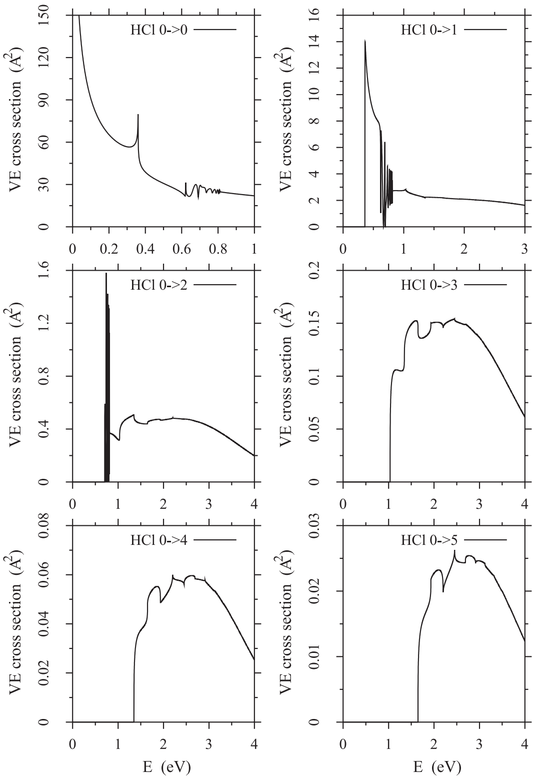

Fig. 3. Vibrational excitation of HCl: $v = 0 \to 0, ..., 5$. Integral cross-sections are given in Å^2.

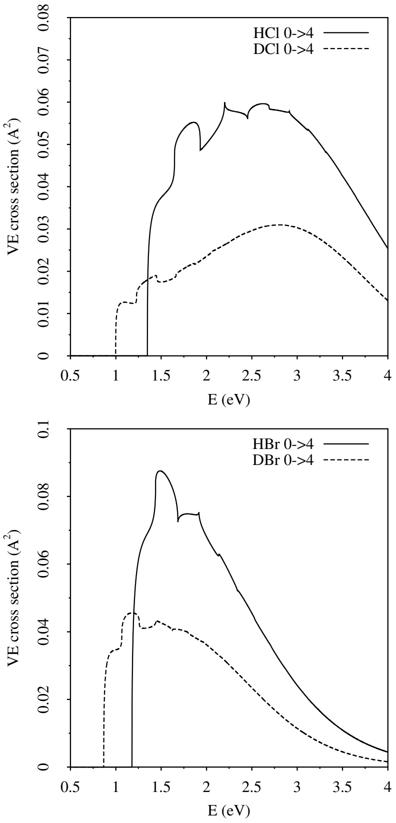

Fig. 4. $v = 0 \to 4$ vibrational excitation of HCl/DCl (left panel) and HBr/DBr (right panel). Integral cross-sections are given in Å^2.

based on the use of the nonlocal resonance model [4] gives at the electron energy 4.0 eV the value of 0.86 which is not far the value 0.71 of Atems and Wadehra). The range of (approximate) validity of equation (6) is however limited to higher energies above 4–5 eV. At lower energies and in close vicinity of the threshold the results obtained by equation (6) may differ significantly from the exact values.

In Figure 4 we show direct comparison of the $0 \to 4$ VE cross-sections for HCl(DCl) and HBr(DBr) molecules. The peak value of the cross-section for the hydrogenated molecule is approximately twice as large as the cross-section for the deuterated molecule. This is true, however, only for initial target states which are well below the DA threshold. As the initial vibrational quantum number v increases, the agreement with the theory of Chang and Wong deteriorates and a new effect is observed: the vibrational excitation cross-section of the heavier molecule may be (significantly) larger than that of the lighter molecule. This phenomenon is exemplified in Figure 5: the VE cross-sections of HCl (HBr) (solid line) are compared with those of DCl (DBr) (dashed line). In the left panel, the VE cross-sections are shown for excitation from the vibrational ground state. These cross-sections follow the rule of equation (6) in so far as the cross-sections of the deuterated compounds are smaller than those of the hydrogenated ones. The dependence of the cross-section ratio on $|v_i - v_f|$, on the other hand, is not in agreement with the simple rule

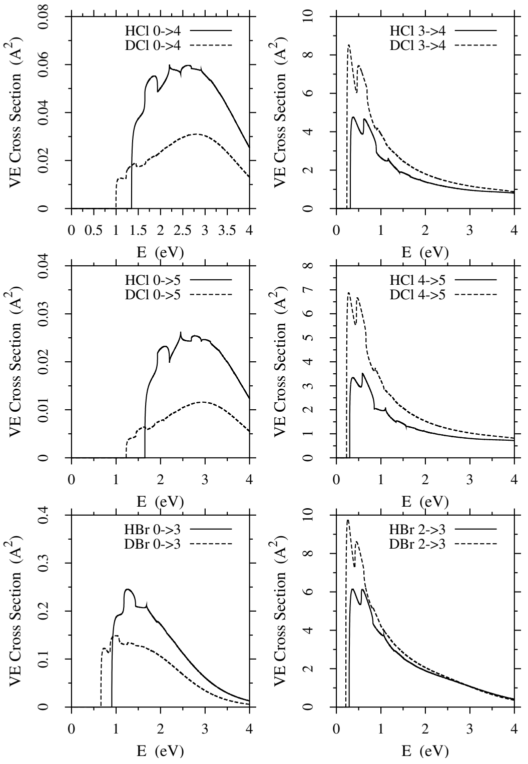

Fig. 5. Vibrational excitation of HCl/DCl and HBr/DBr molecules to a given final state. Left panel: VE from the ground vibrational state; right panel: VE from vibrationally excited molecules. HCl/HBr: solid lines; DCl/DBr: dashed lines. In the left panel, the VE cross-sections of HCl(HBr) are larger than those for DCl(DBr). In the right panel the VE cross-sections for the deuterated molecules are larger than that of the hydrogenated molecules (inverse isotope effect).

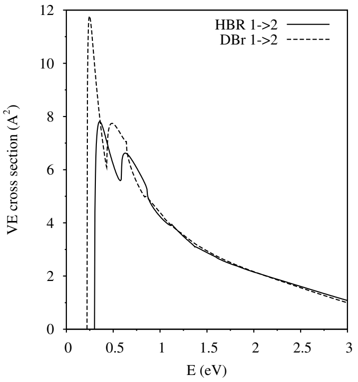

Fig. 6. Vibrational excitation 1 → 2 of HBr/DBr molecules. The initial vibrational states lie energetically below the DA threshold.

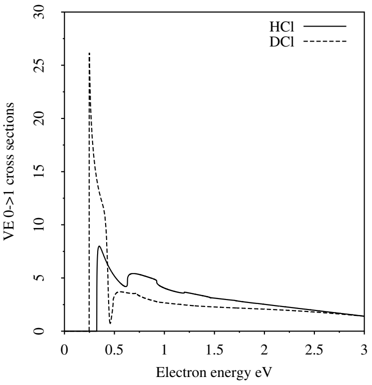

Fig. 7. 0 → 1 vibrational excitation of rotationally excited ($J = 30$) HCl/DCl molecules, revealing an inverse isotope effect.

of equation (6). In the right panel, VE cross-sections are shown with the same final vibrational channel as in the left panel, but for initially excited vibrational levels. In the whole energy range the VE cross-sections of the hydrogenated molecules are smaller than those of the deuterated counterparts. In analogy with DA, we refer to this effect as "inverse isotope effect". This effect occurs when the initial vibrational target state is above the threshold energy for DA (in the case of HCl, the DA threshold lies between $v = 2$ and $v = 3$, in the case of HBr between $v = 1$ and $v = 2$, see Fig. 1). In some cases, however, the effect is observable also for states which lie energetically below but close to the threshold energy of DA, see Figure 6.

The inverse isotope effect in VE may qualitatively be interpreted in terms of the lifetime of the collision complex. Since the initial as well as the final states are energetically close to the energy of the resonance (discrete) state which is responsible for the inelastic process, it is reasonable to assume that the lifetime of the collision complex is very short compared with the time the nuclei need to slide down on the resonance potential to reach the point of electronic stabilization of the anion. In the present case of VE of vibrationally excited molecules, the time the nuclei spend moving on the resonance potential is so short that the difference in mass (and in speed) plays only a minor role, and other effects become more important. This is supported by the fact that for deeper inelasticity (transitions $v \rightarrow v + 2$, $v \rightarrow v + 3$, etc.) the inverse isotope effect gets less and less pronounced and eventually turns over to the normal one. The same holds also for superelastic scattering, $v \rightarrow v - 2$, etc.

In addition to VE, also pure rotational excitation may lead to the inverse isotope effect. In Figure 7, we show the 0 → 1 VE cross-section for HCl and DCl molecules in their ground vibrational state, but highly excited rotational state ($J = 30$). The inverse isotope effect occurs within the threshold peak.

3.2 Dissociative attachment

The calculated DA cross-section of DCl in its ground rovibrational initial state is shown in Figure 8. Wigner cusps at the opening of the vibrational excitation channels are clearly discernible.

In any real experiment, the target gas is at a finite temperature T and the electron beam has a finite energy resolution ΔE. In Table 1, the peak values of the DCl DA cross-sections are given for a set of temperatures T

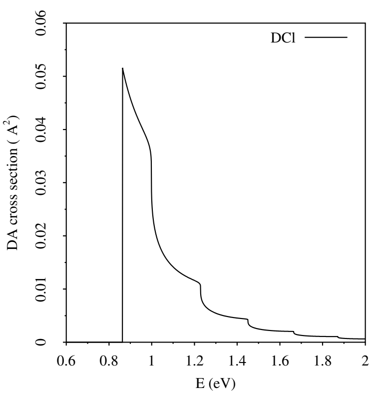

Fig. 8. Dissociative attachment of cross-section of DCl in its ground rovibrational state.

Table 1. Dissociative attachment peak cross-sections for DCl calculated at a temperature T for two electron beam energy resolutions. Second and third column: peak energy and peak cross-section calculated for the energy resolution $\Delta E = 10$ meV. Columns four and five: the same for the energy resolution 100 meV.

T (K)	E_{10} (eV)	Q_{10}(Å^2)	E_{100} (eV)	Q_{100}(Å^2)
100	0.880	4.76(−2)	0.930	3.84(−2)
200	0.880	4.81(−2)	0.925	3.96(−2)
300	0.875	4.87(−2)	0.920	4.06(−2)
400	0.785	4.94(−2)	0.915	4.17(−2)
500	0.875	5.03(−2)	0.910	4.28(−2)
600	0.875	5.16(−2)	0.905	4.44(−2)
700	0.875	5.34(−2)	0.900	4.64(−2)
800	0.875	5.57(−2)	0.895	4.90(−2)

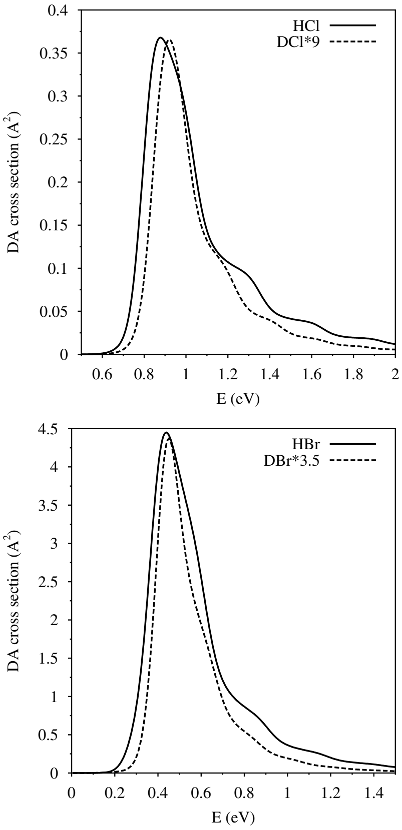

Fig. 9. Isotope effect in DA of DCl/HCl (left panel) and DBr/HBr (right panel). Cross-sections are given in Å^2. The temperature of the target gas is $T = 300$ K, beam energy resolution is $\Delta E = 100$ meV. The DA cross-section of DCl has been multiplied by a factor of 9 and that of DBr by a factor of 3.5.

ranging from 100 K to 800 K and for two electron beams: a beam with high energy resolution ΔE(FWHM = 10 meV) and a beam with low energy resolution ($\Delta E = 100$ meV). It is seen that the magnitude of the peak cross-section increases with increasing temperature, while it decreases with increasing width of the electron beam.

The isotope effect in DA of HCl/DCl was discussed in [16]. It was found that the peak DA cross-section calculated at zero temperature (i.e., $J = 0$, $v = 0$) of DCl is about ten times smaller than the peak cross-section of HCl [16]. In the case of HBr/DBr, the ratio equals approximately five [4]. However, this value cannot directly be measured. In a real experiment, the molecule is at a finite (room) temperature and the cross-section must be averaged over all molecular states populated at this temperature. Moreover, the energy resolution of the incident electron beam must be taken into account by convoluting the temperature averaged cross-sections with the electron beam distribution. Both features have a significant effect on the magnitude of the isotope effect (see Tab. 1).

In Figure 9, DA cross-sections at the temperature 300 K and energy resolution 100 meV are shown for HCl and DCl (upper panel). In this figure, the DA cross-section of DCl was multiplied by a factor of 9. Analogous cross-sections for HBr and DBr are shown in the lower panel of Figure 9. Here, the DBr cross-section was multiplied by a factor of 3.5. According to our calculation, the DA cross-section in HCl is thus approximately nine times larger than in DCl in the energy region where the cross-section is large.

The only experimental data for HCl we are aware of is a ratio of 1.4 reported by Christophorou et al. [17] and 4.9 by Azria et al. [18]. A calculation of Teillet-Billy and Gauyacq [19] found an isotope effect even larger than ours, namely a ratio of 14.3. A pronounced isotope effect is to be expected because of the very short lifetime of the negative ion state involved in the process. The present prediction of the isotope ratio was obtained with no adjustable parameters and should be tested by additional measurements.

4 Discussion

Our calculations predict an unexpected isotope effect which does not seem to have a classical analogue: at the same collision energy the VE cross-section of the heavier (deuterated) compound is larger than the cross-section of the of the lighter (hydrogenated) compound. This phenomenon is observed when the initial target state is energetically close to the threshold of DA. This prediction awaits a confirmation by experiment. The explanation of the inverse isotope effect in VE is not as simple as for DA. It seems that a strong coupling of DA and VE channels is responsible for this phenomenon but other processes may become important. One may envisage, for example, that the lowering of the VE threshold for deuterated molecules may play a role (this is suggested by the fact that the difference between VE cross-sections for DX and HX is largest at the threshold). The magnitude of the cross-section is very sensitive to the position of the threshold on the energy scale. Another feature that obviously plays a role is that for vibrationally or rotationally excited molecules the range of accessible internuclear distances is larger than that of the ground state molecules. The particles probe different regions and are influenced by different interactions. In our understanding the inverse isotope effect is a complex combination of several strongly coupled features.

In a more general context, one can expect that the inverse isotope effect can be found in other molecules as well and may be a general feature of resonance vibrational excitation processes. From the experimental point of view, it is difficult to prepare beams of molecules in vibrationally excited states to carry out inelastic electron collision experiments. For some molecules, however, the inverse isotope effect might be seen even for molecules in their ground vibrational state. An example may be hydrogen iodide. In the latter case, however, the theory predicts only a small difference between the VE cross-sections of HI and DI [5].

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