THEORY OF ELECTRON-MOLECULE COLLISIONS IN THE SUB-meV RANGE

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We discuss the role of the long-range dipolar and polarization interactions in electron collisions with molecules in sub-meV range. These interactions can support weakly bound or virtual states which lead to strong enhancement of cross sections for inelastic scattering . Polarization interaction can also strongly enhance electron attachment to molecules.. We analyze a simple model for electron capture for several molecules.

Introduction

Low-energy electron-molecule collisions are strongly affected by long-range dipolar and polarization interactions. While this influence has been quite well studied for elastic scattering, the role of the long-range interaction in inelastic and reactive collisions is not well understood yet. The present paper discusses two aspects of this problem. First, we analyze the role of weakly bound and virtual states which are supported by the long-range interaction. Secondly we discuss the role of polarization interaction in the process of electron attachment to molecules and analyze the validity of the Vogt-Wannier model [1] for description of this process.

Role of weakly bound and virtual states

The ability of dipolar systems to support weakly bound negative-ion states has been under discussion since the pioneering work of Fermi and Teller [2]. Theoretically, any stationary dipole with a supercritical dipole moment (D>0.6395 a.u.) supports an infinite number of negative-ion states. However, in real molecules the number of these states is finite because of rotations. Moreover, some molecules, like HF and H_2O, do not have stable anion states at all, although their dipole moments are supercritical. Based on results of model calculations for several molecules, Crawford and Garrett [3] concluded that the electron affinity of a polar molecule is positive if its fixed-nuclei value exceeds 0.1 of the rotational constant. Otherwise the bound state disappears and becomes a virtual state. The existence of a virtual (or weakly bound) state introduces a pole in the scattering S matrix as a function of the electron momentum k. If the rotational coupling is weak, the pole lies on the imaginary axis, and the inelastic cross section is given by the well-known equation [4] for scattering by a weakly bound or virtual state. This equation was successfully applied [5] to description of collisional ionization of Rydberg atoms by polar molecules. For very high principal quantum numbers n the Rydberg electron can be treated as a quasi-free particle [6]. The ionization process can be described in this case in terms of the energy transfer from the rotationally excited molecule to the free electron. This means that the rotational deexcitation cross section should be simply averaged over the electron momentum distribution in the Rydberg atom. This procedure allowed us to make reasonable estimates [5] for the energies of bound and virtual dipole-supported states.

Generally for rotationally inelastic scattering the coupling between the initial and final channels might be significant. In this case the S-matrix pole moves off the imaginary axis in the complex **k** plane, and the rotational deexcitation cross section becomes [7]

$$\sigma = \frac{a}{k\left(k^2 + \left|k_p\right|^2 - 2k \operatorname{Re} k_p\right)} \quad ,$$

where k_p is the position of the S-matrix pole, and a is a constant. Typically many rotational states are populated, and we need to know the dependence of k_p and a on rotational quantum numbers. This dependence can be investigated by solving rotational close coupling equations with a model potential whose long-range part properly describes all long-range interactions and the short-range part is adjusted to reproduce the experimentally observed rates for collisional ionization of Rydberg atoms. In the meV and sub-meV energy region the de Broglie wavelength of the electron is large compared to the radius of the short-range interaction. Therefore the short-range part is effectively controlled by one parameter which is equivalent to the scattering length for scattering by a short-range potential.

The analysis of sub-meV electron scattering, based on solution of rotational close-coupling equations, was performed for HF [7] and CH_3Cl [8] molecules. Both molecules possess supercritical dipole moments, but do not support bound states. The virtual-state energy of HF^- in its ground rotational state is about 1.3 meV whereas for CH_3Cl^- the corresponding energy is 0.03 meV. For rotationally excited states the S-matrix poles move off the imaginary k axis. Their positions in the complex k plane were calculated in Ref. [9] for the HF molecule and in Ref. [8] for CH_3Cl. (All numbers are given for the equilibrium internuclear separations.) Note that these poles do not correspond to resonance states: there is no time delay in scattering, and they do not lead to the Breit-Wigner form of the scattering cross section. However, they can strongly influence the magnitude of the cross section at low energies. As the degree of rotational excitation increases, the poles move farther from the origin, and their influence becomes weaker [9].

Role of polarization interaction in electron attachment

Electron attachment to molecules might be strongly influenced by the polarization interaction. Klots [10] proposed to use the Vogt-Wannier (VW) model [1] for capture into polarization well to describe electron attachment. This model assumes that the capture occurs with 100% probability if the electron falls into the singularity created by the polarization potential $-\alpha/2r^4$. The cross section depends only on energy E and polarizability α, and in the low-energy region it is given by a simple equation

$$\sigma = 4\pi\left(\alpha/2E\right)^{1/2} \quad .$$

The VW model seems to be unphysical in the sense that the actual long-range potential does not have a $1/r^4$ singularity. In order to analyze the validity of the VW model, we have applied it to calculation of the attachment cross section for SF_6 (44.1), CCl_4 (75.6), and C_{60} (558), where we indicate the polarizabilities in a.u. in parentheses.

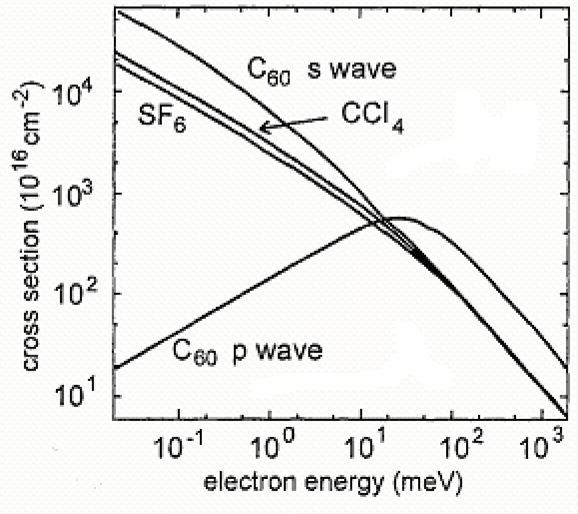

Fig. 1. The Vogt-Wannier attachment cross section for several molecules

The results of calculations are plotted in Fig. 1. The WV theory for SF_6 gives a good description of the experimental data [11] up to the threshold for vibrational excitation.

For CCl_4, the theoretical zero-energy capture rate coefficient, 6.74×10^{-7} cm^3/s, is substantially lower than the latest experimental value, 12.3×10^{-7} cm^3/s [12]. However, the overall behavior of the attachment cross section is described quite well by the VW curve.

The success of VW model for SF_6 and CCl_4 supports the idea [13] of the direct (versus the resonant) capture mediated by a virtual state. The low-energy electron can give up its energy to become bound if the crossing of the negative-ion curve with the neutral curve occurs close to the equilibrium internuclear separation. However, there should be a mechanism preventing the electron from escaping into the continuum. In the case of SF_6 this occurs due to a fast redistribution of the available energy over many vibrational modes, before the nuclear framework can oscillate back in its final configuration [13].

A similar situation is likely to occur in attachment to C_{60} in the meV and sub-meV energy range. The calculated s-wave capture rates in this region agree quite well with the experimental data [14] on Rydberg electron transfer. However, comparison of absolute values of rate coefficients shows that the efficiency of the capture in this case is much lower: the VW cross section should be multiplied by a factor of the order of 0.01 to get a reasonable agreement with experimental data.

At the energies above 4 meV the p-wave capture mediated by a resonance of symmetry t_{1u} [15] becomes more efficient. Experimental data [16] on electron capture by C_{60} in the energy range up to 0.5 eV are well described by the p-wave capture model. Earlier flowing afterglow measurements [17] show the activation barrier of 0.26 eV for the capture process which was interpreted in terms of elastic scattering model [18]. However, this model gives a wrong energy dependence for the p-wave capture cross section, E^2 instead of $E^{1/2}$. As can be seen from Fig. 1, the VW p-wave cross section peak at much lower energy, 0.026 eV. This is in good agreement with the beam experiment [16], but does not explain the temperature dependence observed in the flowing afterglow experiment [17]. We believe that the observed temperature dependence is due to internal excitations in the target.

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ТЕОРІЯ ЕЛЕКТРОН-МОЛЕКУЛЯРНИХ ЗІТКНЕНЬ У СУБМІЛІЕЛЕКТРОНВОЛЬТНОМУ ДІАПАЗОНІ

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Обговорюється роль далекодіючих дипольних і поляризаційних взаємодій у зіткненнях електронів з молекулами у субміліелектронвольтному діапазоні. Ці взаємодії можуть підтримувати слабо зв'язані чи віртуальні стани, що веде до сильного зростання перерізів для непружного розсіювання. Поляризаційна взаємодія може також сильно посилювати прилипання електронів до молекул. Аналізується проста модель захоплення електрона деякими молекулами.