Elastic low-energy electron collisions with methylamine

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Abstract. We present *ab initio* scattering calculations results of low-energy electron collision with methylamine using *R*-matrix approach within the static-exchange (SE) and static-exchange-polarization (SEP) approximations. The elastic integral, momentum transfer and differential cross sections are reported. The calculated elastic integral cross sections are in agreement with the available experimental and theoretical data. A σ^* shape resonances of $^2A'$ symmetry located at 8.9 eV are detected within SEP model. For this dipole molecule Born-closure procedure was used to account for the higher partial waves ($l > 4$) to obtain the convergence of the cross section.

1 Introduction

Studies of low-energy electron collisions with molecules are motivated by their importance in the understanding of radiation damage [1], in the investigating physic-chemistry of interstellar and plasma-based processing. Methylamine, like ammonia, is a molecule of fundamental interest in photochemistry. It is a low-energy source of the fluorescent NH_2 and NH radical species. It has been included in models of the atmospheres of Uranus and Saturn [2-3] and detected in that of Halley's comet [4].

A variety of experimental studies on electron collisions with methylamine are available with some theoretical work. In early experiments, Schmieder and Elektrochem [5] investigated total electron cross section of methylamine. Subsequently, Szmytkowski and Krzysztofowicz [6] measured total cross sections for methylamine in a linear electron-transmission experiment for impact energies from nearly 1 eV up to 250 eV. Samardzic

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et al. [7] measured the complete valence shell electron separation energy spectra and momentum distributions for methylamine by high-resolution electron momentum spectroscopy at a total energy of 1500 eV. Recently, Silva *et al.* [8] investigated low-energy electrons and positrons scattering by methylamine using the Schwinger multichannel (SMC) method. They presented integral (ICS), momentum transfer (MTCS) and differential cross sections for positrons and electrons collision with methylamine. And they found a σ^* shape resonance at around 9.0 eV.

In the present paper we report *R*-matrix calculations of elastic collision with methylamine. We present both differential and integral cross sections at energies ranging from 0.01 to 20 eV. The electron scattering calculations are performed at static exchange (SE), static-exchange-polarization (SEP) using UK molecular *R*-matrix code [9-10]. This method has been proven to be a reliable method to study electron scattering in the low energy region [11-14]. During the course of electron-molecule scattering, the formed shape resonances which can cause enhancements in the cross sections are explored. The differential cross sections are calculated using the code POLYDCS [15].

2 Method

2.1 Theory

The UK molecular *R*-matrix method has been described carefully elsewhere [11], thus here we just present some relevant details of the calculations. This method is a variational technique that relies on the partitioning of configuration space into an inner and an outer part. The boundary is a sphere whose center is located at the center of mass of the molecule. The radii is chosen so that the molecular electron cloud is fully contained within the sphere. In the inner region, exchange and electron-electron correlations are considerable. As a result, the collision problem within a finite volume can be treated as a molecular bound state problem, by constructing and diagonalizing a Hamiltonian matrix. To meet the boundary conditions, the Bloch operator is added to the diagonalized inner region Hamiltonian. In the outer region, exchange and electron-electron correlations are not important and are negligible, and one need only account for the long-range multi-polar interactions between the scattering electrons and the target. Hence the problem can be reduced to solving a set coupled second order equations, which is in practice done by propagating the *R*-matrix and matching to the asymptotic expansion of the solution to obtain the scattering observables.

In inner region, the wave function of the scattering system is written using the configuration interaction (CI) expression

$$\psi_k^{N+1} = A \sum_{ij} a_{ijk} \phi_i^N(x_1, \cdots, x_N) u_{ij}(x_{N+1}) + \sum_i b_{ik} \chi_i^{N+1}(x_1, \cdots, x_{N+1}) \tag{1}$$

where A is an antisymmetrization operator, x_N is the spatial and spin coordinate of the Nth electron, ϕ_i^N represents the ith state of the N-electron target, μ_{ij} is a continuum-

orbital spin coupled with the scattering electron, and k refers to a particular R-matrix basis function. Coefficients a_{ijk} and b_{ik} are variational parameters determined as a result of the matrix diagonalization. The sum in the second term of Eq. (1) represents the short-range correlation and polarization effects, running over all configurations χ_i^{N+1} that are L^2 functions. These are also important for relaxing the orthogonality imposed between the target and continuum orbitals. Gaussian-type orbitals (GTOs) were used to represent the target molecular orbitals.

2.2　Calculation details

All calculations were performed using the nuclei-fixed approximation and the methylamine molecule is described in their ground state using Hartree-Fock self-consistent-field (HF-SCF) with cc-pVTZ basis set. The geometry optimised with B3LYP/6-311+G** method are employed in the present calculations. It is a close shell molecule with C_s symmetry in its equilibrium geometry, and its ground state is ^{1}A' electronic state. Our calculation predicts a permanent dipole moment of 0.517 a.u. which is in good agreement with the experimental value of 0.515 a.u. [16].

The scattering calculations are performed at the static-exchange (SE) and static-exchange plus polarization (SEP) levels. The radius of R-matrix is $12a_0$, which has been proved to achieve a good computational convergence in comparison with that using the larger radius. In the present SEP calculations, the L_2 configurations in Eq. (1) can be written in two classes, (core)^6(valence)^{12}(virtual)^1 and (core)^6(valence)^{11}(virtual)^2. And 40 MOs of A' symmetry (8a' $\sim$ 47a') and 20 MOs of of A" symmetry (3a" $\sim$ 22a") are selected as virtual orbitals. The continuum orbitals up to $l = 4$ (g-partial waves) are represented by GTO. The partial waves for $l > 4$ are included using a Born correction via a closure approach [17] at all energies.

3　Results and discussion

3.1　Elastic integral cross sections

In Fig. 1 we present our calculated elastic integral cross sections of methylamine in SE and SEP models based on the cc-pVTZ basis set, in comparison with the experimental data from Szmytkowski *et al.* [6]. As shown in the figure, SE model predicts a broad peak at about 13.0 eV in total cross section. The position of this peak goes down to 8.9 eV for our SEP model, which is close to the experimental datum 8.5 eV [6]. By analyzing the two components (^{2}A' and ^{2}A") of the total elastic cross section, we find the peak mainly comes from the ^{2}A' symmetry. Through fitting the eigenphase sum to a Breit-Wigner profile [18, 19], one usually can obtain the energy position and the width of the resonance. The resonance with ^{2}A' symmetry locates at 8.9 eV is a shape resonance with a width of 1.8 eV. The SEP results with the Schwinger multichannel (SMC) method from Silva *et al.* [8] are also shown in the picture for comparison. Our total cross section is higher than that of
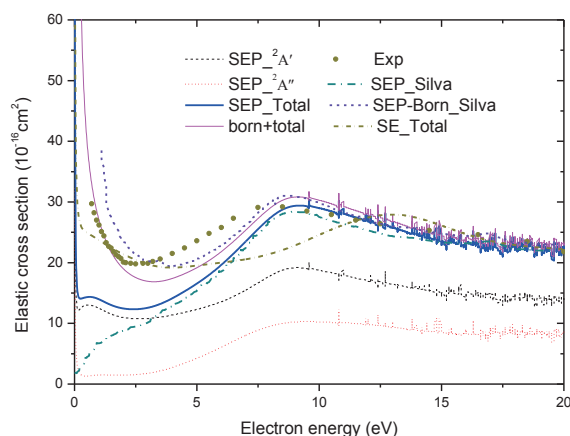
Figure 1: (Color online) SE and SEP models calculated integral cross sections, experimental total cross section from Szmytkowski *et al* [6] and theoretical form Silva *et al* [8] for comparison.

SMC method, especially at low energy region. Considering the polarity of methylamine, it is reasonable that the cross section increases at low energy region.

To obtain converged cross sections, the effect of rotation can be included along with a very large number of partial waves using closure approach [18]. The Born corrected cross section is also shown in Fig. 1. In general, Born corrected cross section is in good agreement with the measured data, except underestimating the cross section in the region from 1.8 eV to 8.0 eV. Born corrected cross section from Ref. [8] shows similar results and also underestimated the cross section in the region from 3.0 eV to 7.8 eV. In the low energy region < 2.8 eV their results overestimated the cross section.

3.2 Differential cross sections

The calculation of the DCSs provides a more stringer test for any theoretical model. Using K-matrix which is obtained from the SEP calculations, DCS is predicted with POLY-DCS program [15]. The calculated dipole moment (0.517 a.u.) and the rotational constants A=3.465 cm^{-1}, B=0.757 cm^{-1} and C=0.726 cm^{-1} at the equilibrium geometry of the ground state of the molecule are used in the calculations of the DCSs (J=0$\rightarrow J'$=0,1, 2, 3,$\cdots$).

Fig. 2 shows our calculated rotationally resolved DCSs for electron scattering by CH_3NH_2 at the incident energy of 2 eV. Since CH_3NH_2 is a strong polar molecule, the 0$\rightarrow$1 contribution is larger than the elastic 0$\rightarrow$0 component at the angles $< 80°$. At the angles $> 80°$, both of them have almost the same intensity. In general, the contribution of the higher J' decreases with the J' increases. We obtained almost convergent results when J' increases up to 5. The DCSs obtained by summarizing the rotational cross sections for (J=0$\rightarrow J'$=0 $\sim$ 5) at the selected energies of 1, 2, 4, 6, 8 and 10 eV are depicted in Fig. 3. The DCSs at all the energies show the sharp increases at the smaller scattering angles for
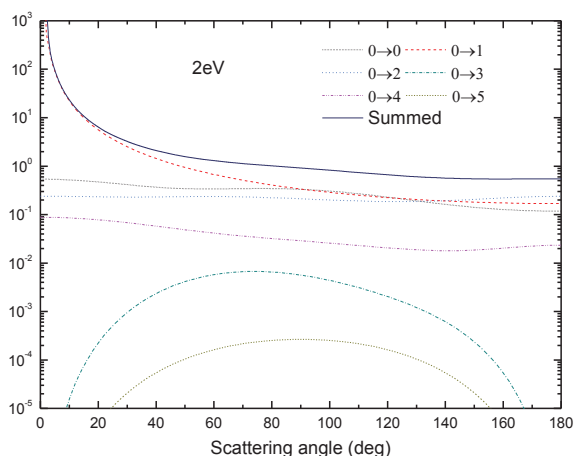
Figure 2: (Color online) Electron impact R-matrix rotationally resolved state-to-state ($J \rightarrow J'$) differential cross sections of methylamine at 2 eV.
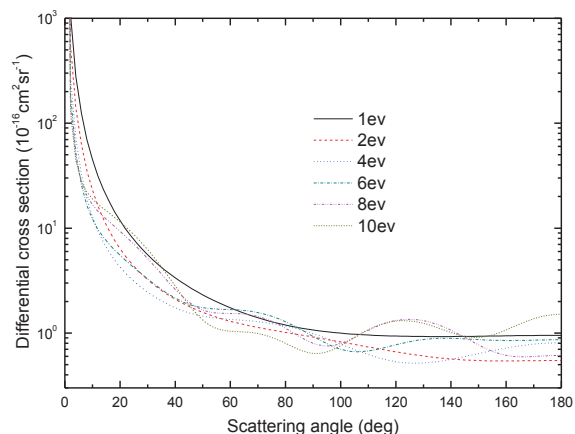

Figure 3: (Color online) Differential cross section (DCS) of methylamine at different energies 1, 2, 4, 6, 8 and 10 eV.

the dipolar nature of the target.

Our calculated momentum-transfer cross section (MTCS) is shown in Fig. 4. The MTCS indicates the weights of backward-scattering and is useful in the study of electrons drifting through a molecular gas. We observe the MTCS decreases with the increasing energy. In contrast to the diverging nature of DCS in the forward direction (at the low scattering angles), MTCS doesn't show exhibit singularity in the forward direction due to the multiplicative factor $(1-\cos\theta)$, where θ is scattering angle. As might be expected from the DCSs, it shows a broad peak about 9 eV. As discussed before, it is due to σ^* shape resonances of $^2A'$ symmetry located at 8.9 eV.
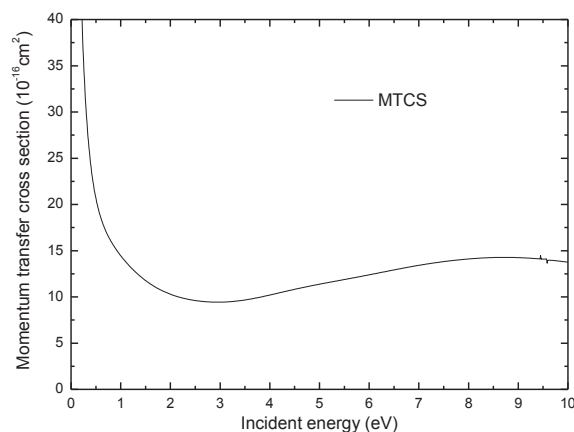
Figure 4: Momentum transfer cross sections of methylamine for energy range of 0.01-10.00 eV.

4 Conclusion

We have calculated the elastic electron-scattering cross section for methylamine molecule using R-matrix method in SE and SEP approximation. The calculated total cross section shows a peak at 8.9 eV, which is due to a σ^* shape resonance of $^2A'$ symmetry with a width of 1.8 eV. Our calculated cross section is in good agreement with the experimental data from Szmytkowski *et al* [6]. The DCS have been used to calculate the elastic momentum transfer cross section. The MTCS plays an important role in the energy distribution during collision.

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