

Resonances in low-energy-electron scattering by nitro compounds

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In this work, we present integral cross sections for elastic scattering of low-energy electrons by the nitro compounds nitroethylene, nitroethane, and 1-nitropropane, for energies up to 8 eV. We calculated the scattering cross sections using the Schwinger multichannel method with pseudopotentials in the static-exchange plus polarization approximation and compared our results with our previous calculations for the nitromethane molecule. Our integral cross sections show π^* and σ^* shape resonances for all compounds, which are important in the understanding of dissociation processes.

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I. INTRODUCTION

Nitro compounds form an important class of energetic materials, used in the industry as explosives, solvents, and fuel additives [1,2]. The covalent C-N bond can be easily broken, so nitro compounds have a tendency to dissociate [3]. Since the decomposition of these compounds occurs at low temperature, they are very unstable molecules and, hence, hard to synthesize. Therefore, the main characteristic that allows these systems to be very important in the combustion process, makes it also difficult to investigate them experimentally. Theoretical studies become particularly relevant in these cases [4].

Nitromethane (CH_3NO_2) is the simplest of these nitro-organic compounds. In a previous work [5], we have already calculated the integral cross section for low-energy-electron collisions with this molecule. We have found a σ^* resonance at 4.8 eV and a π^* resonance at 0.7 eV, in good agreement with the available electron transmission spectroscopy data [6]. The resonance in 0.7 eV also agrees well with the dissociative electron attachment (DEA) peak observed for the NO_2^- fragment located between 0.5 and 0.72 eV [7]. This agreement in the DEA indicates an indirect dissociation pathway through the crossing between the π^* and the σ^* potential-energy surfaces. But, it is also possible that a direct dissociation occurs, with the electron being captured by the 4.8 eV σ^* resonance. Therefore, a thorough description of the collision process can give us helpful information regarding the position of the dissociation peaks and its pathways.

To the best of our knowledge, there are few studies on nitro-compound molecules. For nitroethane, Pelc *et al.* [8] measured the DEA cross section below 10 eV and found a variety of negative ions. They observed resonances at 0.75, 4.5, and 8.5 eV. They associated the peak at 0.75 eV with the resonance at 0.6 eV in nitromethane [7], as attributed to electron capture into the lowest virtual molecular orbital with a localized NO antibonding character and formation of the NO_2^- .

In another study, Lunt *et al.* [9] measured integral scattering cross sections from 30 meV to 1 eV for nitromethane and nitroethane. They did not observe any structure at this energy range, probably due to the large dipole moment of these molecules. According to Lunt *et al.* [9], the cross sections for nitroethane and nitromethane have the same behavior.

The aim of this work is to identify the resonances in the cross sections of the nitro compounds, such as nitroethy-

lene ($\text{C}_2\text{H}_3\text{NO}_2$), nitroethane ($\text{C}_2\text{H}_5\text{NO}_2$), and 1-nitropropane ($\text{C}_3\text{H}_7\text{NO}_2$), as a first step to a further understanding of the DEA process in these systems. We employed the Schwinger multichannel (SMC) method with pseudopotentials (SMCPP) in the static-exchange plus (SEP) polarization approximation to compute integral cross sections, and found the positions of the σ^* and the π^* resonances for all molecules.

This paper is organized as follows. In Sec. II, we present a brief description of the theoretical formulation and the computational procedures. In Sec. III we present our results and discussion.

II. THEORY AND COMPUTATIONAL DETAIL

The SMC method [10–12] and its implementation with pseudopotentials (SMCPP) [13] have been described in detail in several publications. Here we will only describe the relevant points concerning the present work. The SMC method is a variational approach to the scattering amplitude that results in the following working formula:

$$f(\mathbf{k}_f, \mathbf{k}_i) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\mathbf{k}_f} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\mathbf{k}_i} \rangle \quad (1)$$

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \quad (2)$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(P\hat{H} + \hat{H}P)}{2} + \frac{(PV + VP)}{2} - VG_p^{(+)}V. \quad (3)$$

In the above equations, $|S_{\mathbf{k}_i}\rangle$ is a solution of the unperturbed Hamiltonian H_0 and is a product of a target state and a plane wave, V is the interaction potential between the incident electron and the target, $\{|\chi_m\rangle\}$ is a set of $(N+1)$ -electron Slater determinants [configuration state functions (CSFs)] used in the expansion of the trial scattering wave function, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$, P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_p^{(+)}$ is the free-particle Green's function projected on the P space.

In static-exchange (SE) approximation, the $(N+1)$ -electron basis is constructed as $|\chi_m\rangle = \mathcal{A}|\Phi_1\rangle \otimes |\varphi_m\rangle$, where

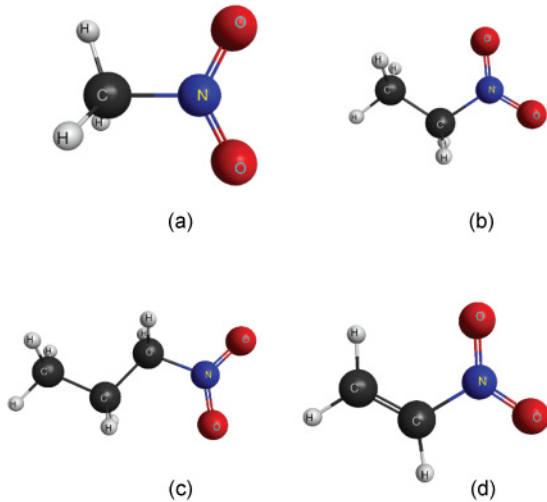


FIG. 1. (Color online) Geometrical structures for (a) nitromethane, (b) nitroethane, (c) 1-nitropropane, and (d) nitroethylene (generated using McMolPlt [17]).

Φ_1 is the Hartree-Fock target ground state and φ_m is a one-particle function. In SEP approximation, the SE set is enlarged by including CSFs constructed as $|\chi_n\rangle = \mathcal{A}|\Phi_m\rangle \otimes |\varphi_r\rangle$, where Φ_m are N -electron Slater determinants which are obtained by performing single excitations on the target, and φ_r is also a one-electron function.

Our calculations were carried out in the static-exchange plus polarization approximation at the optimized ground-state equilibrium geometry. We optimized the geometry at the second-order Møller-Plesset (MP2) level of approximation employing the computer program GAMESS [14]. All the nitro compounds were treated as C_s molecules, and their structures are shown in Fig. 1. We used the pseudopotentials of Bachelet, Hamann, and Schlüter [15] to replace the core electrons of carbon, nitrogen, and oxygen. The one-particle basis set used to represent the target ground state and the scattering orbitals is the same as that used in [5]. The symmetric combinations of the d -type functions were not included in our calculations to avoid linear dependency in the basis set.

To take polarization effects into account we employed the improved virtual orbitals (IVOs) [16] with energies less than 1 hartree to represent particle and scattering orbitals. For A' symmetry we considered all singlet-coupled and triplet-coupled excitations, retaining only doublets [18], and obtained 5987 CSFs for nitroethylene, 7201 CSFs for nitroethane, and 8615 CSFs for 1-nitropropane. In order to avoid overcorrelation, we considered only singlet-coupled excitations for the A'' symmetry, obtaining 2626 CSFs for nitroethylene, 3224 CSFs for nitroethane, and 3981 CSFs for 1-nitropropane, as done in [5].

III. RESULTS AND DISCUSSION

In Fig. 2, we show the integral cross section (ICS) for the A' symmetry. The broad structure present in the ICS for all molecules is a σ^* resonance around 4.9 eV for nitroethane, 5.5 eV for 1-nitropropane, and 5.0 eV for nitroethylene. The positions of these resonances are close to the one

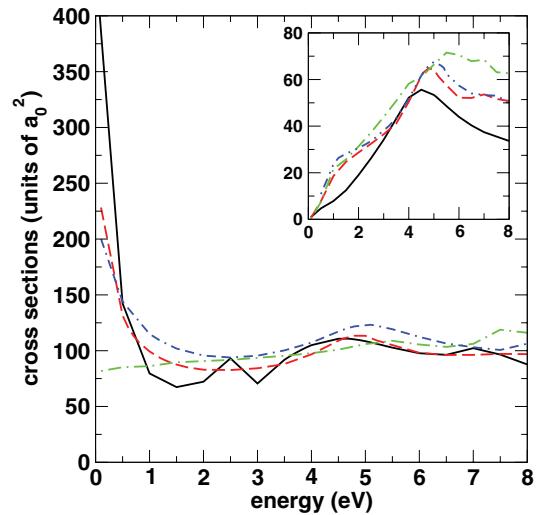


FIG. 2. (Color online) Integral cross section in A' symmetry for nitromethane (black) solid line, nitroethane (red) dashed line, 1-nitropropane (green) dot-dashed line, and nitroethylene (blue) dot-dashed-dashed line. The inset shows the sum of the partial waves that most contribute to the resonance of each nitro compound. See text for discussion. Cross sections are in units of a_0^2 , where a_0 is the Bohr radius and $1a_0 = 0.52918 \times 10^{-10}$ m.

in nitromethane, which is located at 4.8 eV. For the A' symmetry, a combination of partial waves with $\ell = 2$ and 3 contributes most to the resonance for nitromethane, while partial waves with $\ell = 2, 3$, and 4 contribute to the resonance for nitroethane, nitroethylene, and 1-nitropropane. The sum of the partial waves that most contribute to the resonance of each molecule is shown in the inset of Fig. 2. According to Pelc *et al.* [8], the dissociation peak at 4.5 eV for nitroethane is associated with an electronically excited state of the nitroethane anion. As suggested for the nitromethane molecule [5], a direct DEA

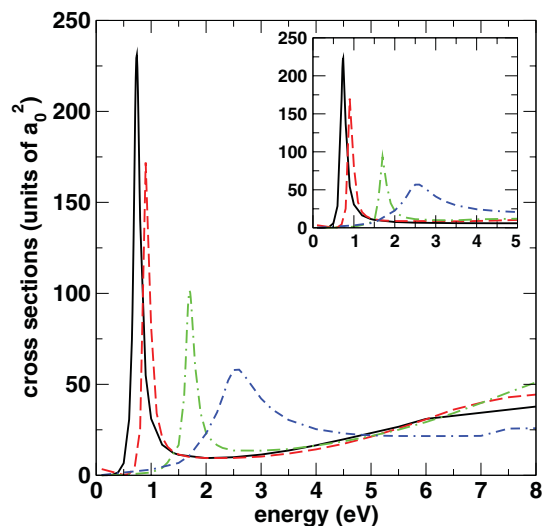


FIG. 3. (Color online) As in Fig. 2 for the A'' symmetry. The inset shows the sum of the partial waves that most contribute to the resonance of each nitro compound. See text for discussion. Cross sections are in units of a_0^2 , where a_0 is the Bohr radius and $1a_0 = 0.52918 \times 10^{-10}$ m.

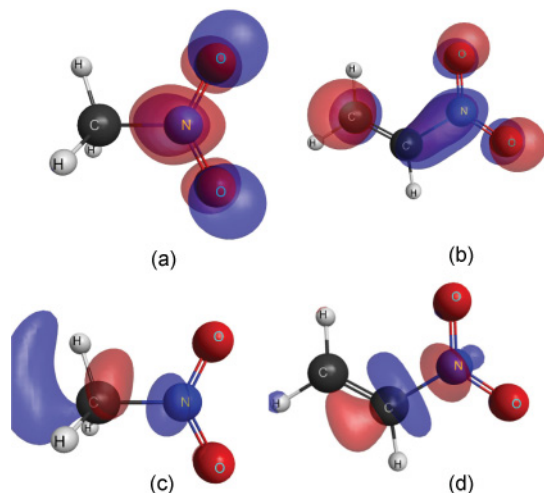


FIG. 4. (Color online) Plots of the LUMO for the π^* orbital of (a) nitromethane and (b) nitroethylene, and of the LUMO + 3 for the σ^* orbital of (c) nitromethane and (d) nitroethylene (generated using McMolPlt [17]).

pathway may also occur at this energy, with the electron being captured at the 4.9 eV σ^* resonance.

We show the ICS for the A'' symmetry in Fig. 3 for energies below 8 eV. We found a π^* resonance at 0.9 eV for nitroethane, at 1.67 eV for 1-nitropropane, and at 2.6 eV for nitroethylene, which are located at higher energies when compared with the π^* resonance of nitromethane (located at 0.7 eV). The partial waves that most contribute to this resonance are $\ell = 1$ for nitromethane, and $\ell = 1$ and 2 for the other nitro compounds (the latter has a bigger contribution for 1-nitropropane). The inset in Fig. 3 shows the sum of the partial waves that most contribute to this resonance for each nitro compound. The π^* resonance at 0.9 eV for nitroethane is close to the DEA peak at 0.75 eV measured by Pelc *et al.* [8], suggesting that the mechanism of NO_2^- formation is probably similar to that of nitromethane.

We also investigated the lowest unoccupied molecular orbital (LUMO) and the LUMO + 3 for the nitro compounds in order to shed some light over the resonance behavior. Figure 4 shows the plots of the LUMO associated to the π^* resonance for nitromethane, which shows the same behavior as nitroethane and 1-nitropropane, and for nitroethylene. The LUMO is located in the NO_2 moiety for nitromethane, nitroethane, and 1-nitropropane. This suggests that the mechanism of the dissociation for nitromethane, nitroethane, and 1-nitropropane is indeed probably the same. We also computed the canonical eigenvalues of the Fock operator using the 6-31G(d) basis set and, using the empirical scaling relations [20], we found for the LUMO the values 0.04, 0.16, and 0.21 eV. These results are significantly lower than the values encountered in this work for the resonance positions. The

LUMO of the nitroethylene molecule, however, is not localized over the NO_2 moiety. The extra double bond delocalizes the state, as shown in Fig. 4. According to the Hückel molecular orbital theory [19], the π state is more stabilized for this heteroatomic conjugated system through the delocalization energy. Henceforth, this effect also raises the energy of the π^* orbital. This delocalization can explain why the resonance for nitroethylene is considerably higher than for the nitroethane molecule. This can be seen by, once again, computing the energy of the molecular orbital and using the empirical scaling relation to obtain 2.25 eV as the position of the resonance. This value is close to the 2.6 eV we have calculated and it is significantly higher than the ones for the other molecules. We also show in Fig. 4 the LUMO + 3 for nitromethane and nitroethylene associated to the σ^* resonance. This figure shows a typical behavior of the LUMO + 3 for all nitro compounds, which is concentrated on the C-N bond. Using the empirical scaling relation [20] the computed energies are 4.43 eV for nitromethane, 3.97 eV for nitroethane, 4.80 eV for 1-nitropropane, and 3.30 eV for nitroethylene.

IV. SUMMARY

We presented elastic cross sections for electron collisions with nitroethylene, nitroethane, and 1-nitropropane, and compared with the results for nitromethane. These calculations show a π^* resonance in the A'' symmetry and a σ^* resonance in the A' symmetry for all the nitro compounds. The resonances for nitroethane and 1-nitropropane are very similar to the one observed for nitromethane. This suggests that the dissociation process is probably very similar for these molecules, as reported in the experimental work of Pelc *et al.* [8]. Indeed, the calculated position of the π^* resonance (at 0.9 eV) is in good agreement with the dissociation peak (at 0.75 eV) seen in [8]. We also observed how the extra double bond in nitroethylene brings the resonance position to higher energies through the delocalization energy [19]. This feature could result in a different DEA mechanism to nitroethylene, which may be interesting for further theoretical and experimental investigations.

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