

# Excited electronic and ionized states of the nitramide molecule, $\text{H}_2\text{NNO}_2$ , studied by the symmetry-adapted-cluster configuration interaction method

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**Abstract** Symmetry-adapted-cluster configuration interaction (SAC-CI) wave functions were employed to compute 16 singlet and 13 triplet vertical transitions, and 14 ionized states including relative intensities of the nitramide molecule,  $\text{H}_2\text{NNO}_2$ . This molecule is the simplest neutral closed-shell molecule which has an N– $\text{NO}_2$  bond and is a member of the nitramine family,  $\text{R,R}'\text{N}(\text{NO}_2)$ , an important class of energetic materials with practical applications. The present nitramide results showed strong similarities with the ones of the *N, N*-dimethylnitramine molecule, which has also an N– $\text{NO}_2$  bond and was previously studied using the SAC-CI method. Experimental ultraviolet and photoelectron band spectra of the nitramide molecule could be successfully assigned. All the singlet transitions have valence character. The computed singlet and triplet transitions, excepting a singlet one, result from excitation originating in the four highest occupied molecular orbitals, which have close energies. Most of the singlet and triplet transitions involved mixing of singly excited configurations. The strongest computed transition, at 6.8 eV, is a mixture of two  $n\pi_{\text{NO}_2} \rightarrow \pi^*$  configurations corresponding to excitations from the highest occupied molecular orbital (HOMO) to the first two virtual orbitals and has an optical oscillator strength value of 0.2665. The computed ionized states described the whole measured spectrum, have excellent agreement when compared with the measured ionization potentials and revealed an inversion of the ordering of the first states not expected according to Koopmann's theorem, thereby showing the limitations of the latter.

**Keywords** Nitramide,  $\text{NH}_2\text{NO}_2$  · SAC-CI wave functions · Excited states · Ionized states · UV spectrum · Photoelectron spectra · Energetic materials

## 1 Introduction

Several molecules containing the  $\text{NO}_2$  group are essential ingredients in many propellants and explosives, which are known as energetic materials. These molecules also present significant biological activity and contribute to the atmospheric pollution [1]. Photochemical processes are important in these systems. Because most nitro-containing compounds have diffuse electronic spectra and tendency to dissociation [2], theoretical investigations about their electronic excited states may be especially important. In particular, nitramines, which general formula is  $\text{R,R}'\text{N}(\text{NO}_2)$ , are one of the most common classes of high-technology energetic materials [3]. They are currently used as military explosives, propellants and fuels. Therefore, theoretical studies can, besides the intrinsic interest in molecular properties, provide important answers to relevant practical questions.

Investigations on gas-phase energetic materials reveal their properties and reactions at the molecular level, and determine the decomposition features as a function of the electronic and vibrational excitations [4]. In particular, the decomposition of energetic materials from their excited electronic states plays an important role in the detonation initiation of these materials [5,6]. As nitro compounds possess strong absorption in the UV region, the detailed knowledge of the molecular electronic excited states can also assist the design of nitro organic explosives detectors [7]. Despite the importance of excited states in energetic materials research, only few studies of them have been carried out [3].

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Nitramide ( $\text{H}_2\text{NNO}_2$ ) is the simplest closed-shell neutral molecule which has an N–NO<sub>2</sub> bond and the simplest member of the nitramine family. This molecule is also a model of the largely used energetic materials RDX (hexahydro-1,3,5-trinitro-*s*-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) [8], which are also members of the nitramines class of molecules. Previous nitramide UV absorption spectra were obtained in the crystal, solution and gas phase [9–11]. The gas-phase UV spectrum shows a moderate band centered around 6.3 eV while the solution spectrum has additionally two weak shoulders below 5 eV. On the theoretical side, there are some old semi-empirical calculations of the nitramide molecule [2,9–11]. Two of these studies conclude that the moderate band is due to the overlap of two bands, but of different character. Nagakura [11] stated that the band is an intra-NO<sub>2</sub> ( $\pi \rightarrow \pi^*$ ) transition and a charge transfer between a donor (NH<sub>2</sub>) and an acceptor (NO<sub>2</sub>) while Stals et al. [10] established it as mixture of  $\sigma \rightarrow \pi$  and  $\pi \rightarrow \pi^*$  configurations. The semiempirical work of Harris [2] computed a  $\pi \rightarrow \pi^*$  transition for the moderate band. Recently, Soto et al. [8] reported ab initio complete active space self-consistent field followed by multistate second-order perturbation theory (MS-CASPT2) calculations of the first four singlet and the first three excited states. They interpreted the gas UV absorption spectrum of nitramide as the overlap of two bands of moderate intensity, centered at 6.46 eV ( $n\pi \rightarrow \pi_{\text{NO}_2}^*$ ) and 6.53 eV ( $n\pi \rightarrow \pi_{\text{NO}_2}^*$ ). They have also computed two more singlet excitations and three triplet excitations.

Attina et al. [1] recorded the photoelectron spectra (PE) of nitramide. The PE show that two broad bands and spectral features due to its decomposition products, N<sub>2</sub>O and H<sub>2</sub>O, are also present in the same spectral region. Below 13 eV, there are two bands centered at 11.28 and 11.69 eV. The two broad bands are separated by about 2 eV. We are unaware of any theoretical works on the ionization spectrum of the nitramide molecule.

In this work, we used the symmetry-adapted-cluster configuration interaction (SAC-CI) wavefunctions [12–15] to compute 16 singlet and 13 triplet transitions, and 14 ionized states. Vibronic effects [16] were not included. Our results were compared with previous theoretical and experimental results.

## 2 Computational details

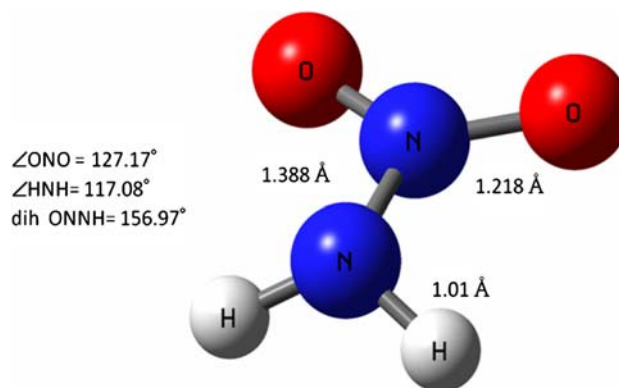
Several singlet, triplet and ionized transitions of the nitramide molecule were computed. Vertical oscillator strengths for the singlet transitions were obtained. The ionization cross sections were calculated in the monopole approximation [17, 18]. This approximation allows the estimation of the relative intensity of the peaks. In calculating the monopole

intensity, the correlated SAC wavefunction was used for the ground state. This approach allowed the inclusion of both initial- and final-state correlation effects. We used the Dunning/Huzinaga valence double-zeta [19] D95V+(d,p) Gaussian basis set with diffuse and *d* polarization functions on the heavy atoms, and *p* functions on the hydrogen atoms. This basis set produced 86 molecular orbitals.

Geometry was optimized through the DFT [20]-B3LYP [21]/aug-cc-pVTZ [22] method without symmetry constraints. The geometry converged to Cs symmetry, which agrees with previous studies [23]. Vibrational calculations were done to check on the minimum character of the optimized structure. The optimized geometry, shown in Fig. 1, was used throughout the SAC-CI ground and excited states calculations.

The symmetry-adapted-cluster (SAC) [13]/configuration interaction (CI) [12, 14, 15] wavefunction was used for the excited state calculations. The SAC-CI wavefunction is based on a cluster expansion of a CI calculation carried out over selected configurations. In this approach, all singly excited configurations are included without selection and the most important doubly excited configurations are treated through linked operators, while triply and quadruply excited configurations, generated by the products of previous single and double excitations, are treated through unlinked operators. The doubly excited configuration operators for the ground and excited states are selected according to perturbation threshold coefficients. Applications of the SAC-CI wavefunctions to a variety of molecular systems are available in the literature [24, 25].

For the calculation of the SAC (ground state) and the SAC-CI (excited states) wavefunctions, all the orbitals were correlated. The active space comprised the full set of 16 occupied orbitals and 70 virtual orbitals. All the singly and selected doubly excited configurations were included in the wavefunction. A perturbation selection scheme was used to select the important doubly excited configurations. The



**Fig. 1** The converged DFT-B3LYP//aug-cc-VTZ geometry for the nitramide molecule

energy thresholds for the perturbation selection procedure, known as level three scheme, were  $1.0 \times 10^{-6}$  and  $1.0 \times 10^{-7}$  a.u. for the ground and excited states, respectively. The oscillator strength calculated in this work employed the dipole representation [26,27]. The Gaussian 03 program [28] was applied to DFT optimization and the SAC/SAC-CI calculations.

### 3 Results and discussion

#### 3.1 Singlet states and electronic excitation spectrum

The nitramide ground state has  $^1A'$  symmetry. This molecule has 32 electrons distributed in the following doubly occupied SCF orbitals, shown in increased energy order:

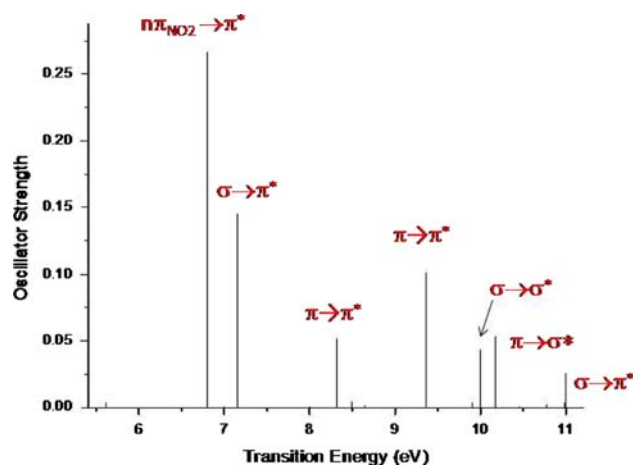
1a'' 2a' 3a' 4a' 5a' 6a'' 7a' 8a' 9a'' 10a' 11a' 12a'' 13a' 14a'' 15a' 16a''

Table 1 identifies the character and energies of the molecular orbitals involved in the studied transitions. The whole computed vertical excitation spectrum is shown in Fig. 2. The four highest occupied orbitals have close energies (Table 1) and, for this reason, the calculated transitions, excepting one, entails configurations with excitations from them. The exception is the  $1^1A' \rightarrow 8^1A''$  transition, corresponding to excitation from the fifth occupied orbital, which is separated from this group of four orbitals by at least 4.7 eV. The five highest orbitals have the following character (the number represents the molecular orbital number): 12 ( $\pi$ ), 13 ( $\sigma$ ), 14 ( $\pi$ ), 15 ( $\sigma$ ), and 16 ( $n\pi_{NO_2}$ ). We have seen an identical

**Table 1** The SCF/D95V+(d,p) main valence molecular orbitals (MOs) of nitramide

MO	Nature	Orbital energy (eV)
12	$\pi$	-19.21
13	$\sigma$	-14.50
14	$\pi$	-13.74
15	$\sigma$	-13.48
16 (HOMO)	$n\pi_{NO_2}^a$	-12.88
17 (LUMO)	$\pi^*$	2.08
18	$\pi^*$	2.38
19	$\sigma^*$	3.45
20	$\pi^*$	3.64
21	$\pi^*$	4.47
22	$\pi^*$	4.75
23	$\pi^*$	5.60
24	$\sigma^*$	5.83

<sup>a</sup> Lone pair type orbital localized in the  $NO_2$  group



**Fig. 2** Computed SAC-CI electronic spectra in the 4.7–11 eV excitation energy interval

situation in SAC-CI calculations of the similar molecule *N,N*-dimethylnitramine,  $(CH_3)_2NNO_2$ , namely: (a) the proximity in energy of four highest occupied energies originates the valence transitions; and (b) the computed transitions involved mixing of singly excited configurations [6].

The calculated nitramide singlet transitions have valence character. This property was verified by comparing the computed second moment values ( $\langle r^2 \rangle$ ) (not shown) of the ground and excited states.

Table 2 collects the SAC-CI computed vertical singlet transitions from the  $1^1A'$  ground state. The gas-phase UV spectrum of nitramide [11] shows a moderate band centered around 6.3 eV and the solution spectrum has additionally two weak shoulders below 5 eV. Our results for the band at 6.3 eV correspond to the overlap of two transitions. The first one, at 6.8 eV,  $1^1A' \rightarrow 2^1A''$ , which is a mixture of two  $n\pi_{NO_2} \rightarrow \pi^*$  configurations with excitations from the HOMO (highest occupied molecular orbital) to the first two virtual orbitals, has an optical oscillator strength value of 0.2665. The strongest transition in the *N,N*-dimethylnitramine molecule is also a mixture of  $n\pi_{NO_2} \rightarrow \pi^*$  configurations [6]. In both molecules, this result, in agreement with experimental results which indicate the labile character of the  $NO_2$  group [3], points to the predominance of an  $N-NO_2$  scission dissociation process. The second transition,  $1^1A' \rightarrow 3^1A'$ , with a transition energy of 7.15 eV, is a mixture of three  $\sigma \rightarrow \pi^*$  excitations and has 0.1450 as oscillator strength. The MS-CASPT2 results of Soto et al. [8] also pointed to the same two transitions for this band, namely, to the  $2^1A''$  and  $3^1A'$  states, but with some differences when compared with ours. Both their transitions have lower computed transitions energies when compared with our values, with a difference of 5% ( $2^1A''$ ) and 9% ( $3^1A'$ ), a rather good agreement. Their oscillator strengths are also lower than ours, but now with larger differences: 36%

**Table 2** SAC-CI computed singlet excited states of nitramide

State	Main configurations ( $ C  \geq 0.30$ )	Excitation energy (eV)	Oscillator strength
$1^1A''$	$-0.56 (14-18) - 0.56 (14-17)$	4.74 (4.50)	0.0 ( $1.7 \times 10^{-6}$ )
$2^1A'$	$-0.62 (13-18) + 0.48 (13-17) - 0.39 (15-18) + 0.30 (15-17)$	5.62 (5.11)	0.0038 (0.0049)
$2^1A''$	$-0.70 (16-18) + 0.58 (16-17)$	6.80 (6.46)	0.2665 (0.1851)
$3^1A'$	$0.57 (15-17) - 0.55 (15-18) + 0.43 (13-18)$	7.15 (6.52)	0.1450 (0.1087)
$4^1A'$	$0.68 (15-17) + 0.62 (15-18)$	8.32	0.0522
$3^1A''$	$0.70 (14-17) - 0.50 (14-18) - 0.34 (14-19)$	8.49	0.0044
$4^1A''$	$0.67 (16-17) + 0.54 (16-18) + 0.35 (16-19)$	8.65	0.0017
$5^1A'$	$-0.69 (13-17) - 0.44 (13-18) - 0.32 (13-19)$	9.36	0.1013
$5^1A''$	$0.89 (15-20)$	9.91	0.0004
$6^1A'$	$-0.69 (15-19) + 0.45 (15-24)$	10.00	0.0435
$6^1A''$	$-0.84 (14-19)$	10.17	0.0538
$7^1A'$	$-0.85 (14-20)$	10.46	0.0001
$8^1A'$	$0.47 (15-19) + 0.42 (13-19) + 0.31 (15-24)$	10.77	0.0026
$7^1A''$	$-0.80 (14-21)$	10.89	0.0000
$8^1A''$	$-0.63 (12-18) + 0.47 (12-17)$	10.98	0.0036
$9^1A'$	$0.67 (15-21) - 0.51 (13-19)$	11.00	0.0258

The label (M–N) indicates the configuration due to excitation from molecular orbital (MO) M to (MO) N. Excitation energies presented in electron volts (eV). The excitation energies and the oscillator strengths values between parentheses are the MS-CASPT2 values computed by Soto et al. [8]. The total SAC  $1^1A'$  ground state energy equals  $-260.292157$  hartrees

( $2^1A''$ ) and 29% ( $3^1A'$ ). The MS-CASPT2 character for both transitions are  $n\pi \rightarrow \pi^*$  singly excited configurations, originating from different lone pair orbitals, while our results mixed  $n\pi_{\text{NO}_2} \rightarrow \pi^*$  excited configurations for the  $2^1A''$  transition and  $\sigma \rightarrow \pi^*$  excited ones for the  $3^1A'$  transition.

We assign the weak shoulder appearing in the solution spectrum to the  $1^1A' \rightarrow 2^1A'$  transition, which is a mixture of four  $\sigma \rightarrow \pi^*$  configurations, with a transition energy of 5.62 eV and an oscillator strength of 0.0039. Soto et al. [8] reached a similar result: one transition, corresponding to a single  $\sigma \rightarrow \pi^*$  configuration with a transition energy 10% lower than ours and a 25% higher oscillator strength value.

Considering the quite different nature of the wavefunctions employed by Soto et al. [8] and by us, the MS-CASPT2 and SAC-CI wavefunctions [29], respectively, the comparison between both sets of results is quite good.

The other 12 calculated singlet transitions, not computed or measured before, are described in Table 2 and shown in Fig. 2. For transition energies greater than 7.15 eV, it can be seen (Fig. 2) that five transitions have appreciable optical oscillator strength values, comparable with the two transitions that comprise the first band. The two most intense transitions of this group, which are to the  $4^1A'$  state at 8.32 eV and to the  $5^1A'$  state at 9.36 eV, are dominated by  $\pi \rightarrow \pi^*$  configurations. Of the remaining three, in order of increasing transition energy, one ( $1^1A' \rightarrow 6^1A'$ ) is a mixture of  $\sigma \rightarrow \sigma^*$  configurations, the other ( $1^1A' \rightarrow 6^1A''$ ) is a  $\pi \rightarrow \sigma^*$  singly excited configuration and the last one ( $1^1A' \rightarrow 9^1A'$ ) is

a mixture of  $\sigma \rightarrow \pi^*$  and  $\sigma \rightarrow \sigma^*$  configurations. It is worth to mention that previous SAC-CI calculations of the *N,N*-dimethylnitramine excited states [6], a molecule also containing an  $\text{NO}_2$  group, have as before similarities with the present nitramine results, namely, the most intense transition is a mixture of  $n\pi_{\text{NO}_2} \rightarrow \pi^*$  excited configurations and the other intense transition involves  $\sigma \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excited configurations.

### 3.2 Triplet states

Thirteen triplet states, and the corresponding transition energies referred to the singlet ground state, were calculated and are shown in Table 3. All the computed transitions are excitations from the four highest excited energy molecular orbitals, which have close energies. This overall pattern of dominant excitations, mostly involving more than one singly excited configuration, is similar to the singlet transitions, and to the previously computed SAC-CI triplet manifold of the similar molecule *N,N*-dimethylnitramine [6].

The first triplet state, the  $1^3A''$  at 4.24 eV, is a mixture of two  $n\pi_{\text{NO}_2} \rightarrow \pi^*$  configurations. Soto et al. [8] computed a MS-CASPT2 excitation energy of 4.29 eV and the same character. They have obtained the second triplet state ( $2^3A''$ ), with 4.32 eV excitation energy, and also  $\pi \rightarrow \pi^*$  character, while we calculated it as 4.52 eV and a mixture of  $\pi \rightarrow \pi^*$  excitations. Their last computed triplet state  $1^3A'$  had an excitation energy of 4.94 eV when compared with our value

**Table 3** Computed triplet excited states of nitramide using the SAC-CI wavefunction

State	Main configurations ( $ C  \geq 0.30$ )	Excitation energy (eV)
$1^3A''$	$-0.74 (16-18) + 0.55 (16-17)$	4.24 (4.29)
$2^3A''$	$0.74 (14-18) - 0.56 (14-17)$	4.52 (4.32)
$1^3A'$	$0.58 (13-18) + 0.47 (15-18) - 0.43 (13-17) - 0.35 (15-17)$	5.37 (4.94)
$2^3A'$	$0.53 (15-18) - 0.48 (15-17) - 0.45 (13-18) + 0.37 (13-17)$	6.37
$3^3A'$	$0.70 (15-17) + 0.57 (15-18)$	7.91
$3^3A''$	$0.68 (14-17) + 0.48 (14-18) + 0.36 (14-19)$	8.40
$4^3A''$	$-0.68 (16-17) - 0.47 (16-18) - 0.39 (16-19)$	8.55
$4^3A'$	$-0.67 (13-17) - 0.50 (13-18)$	9.17
$5^3A'$	$0.52 (15-24) - 0.50 (15-19) + 0.33 (15-32)$	9.41
$5^3A''$	$-0.86 (15-20) - 0.31 (15-22)$	9.86
$6^3A''$	$0.84 (14-19)$	9.98
$7^3A''$	$-0.82 (16-19)$	10.11
$6^3A'$	$0.87 (16-20)$	10.32

The excitation energies refer to the singlet ground state. The label (M–N) indicates the configuration due to excitation from MO M to MO N. The excitation energies between parentheses are MS-CASPT2 values computed by Soto et al. [8]

of 5.37 eV and the same  $\sigma \rightarrow \pi^*$  character. Our next state ( $2^3A'$ ) at 6.37 eV is a mixture of  $\sigma \rightarrow \pi^*$  configurations. The obtained nine remaining states are separated from the first four by at least 1.5 eV, have very close energies and  $\sigma \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ,  $n\pi_{\text{NO}_2} \rightarrow \sigma^*$  and  $\sigma \rightarrow \sigma^*$  character. Therefore, the triplet manifold can be considered as divided into two sub-manifolds. The *N,N*-dimethylnitramine molecule [6] has also a similar division of the triplet manifold, transition energies and overall excitation character.

### 3.3 Ionized states

We calculated 14 ionized states of the nitramide molecule, including the relative peak intensities in the monopole approximation. Our results and the experimental ionization energies [1] are shown in Table 4.

The first eight ionized states are dominated by singly ionized configurations. There is another ionized state dominated by a single ionization ( $6^2A'$ ), and it is interesting to note that

**Table 4** Computed SAC-CI ionization potentials (IP) in eV, monopole intensities and main configurations of the ionized states of nitramide

Symmetry	IP	IP (exp) <sup>a</sup>	Intensity	Main configurations
$1^2A''$	11.39	11.28	0.912	$0.95 (14a'')^{-1}$
$2^2A''$	11.64	11.69	0.918	$0.96 (16a'')^{-1}$
$1^2A'$	11.81	11.75	0.922	$-0.91 (15a')^{-1}$
$2^2A'$	12.42	12.47	0.916	$-0.91 (13a')^{-1}$
$3^2A''$	17.14	17.23	0.917	$0.93 (12a'')^{-1}$
$3^2A'$	18.29	18.33	0.810	$0.89 (11a')^{-1}$
$4^2A'$	19.15	19.58	0.875	$-0.92 (9a'')^{-1}$
$4^2A''$	19.78		0.928	$0.93 (9a'')^{-1}$
$5^2A'$	21.11		0.00248	$0.53 (14a'')^{-1}(16a'')^{-1}(18a')^1 + 0.48 (13a')^{-1}(15a')^{-1}(17a')^1 + 0.39 (14a'')^{-2}(18a')^1$
$5^2A''$	21.94		0.0114	$0.71 (15a')^{-1}(16a'')^{-1}(18a')^1 - 0.53 (15a')^{-1}(16a'')^{-1}(17a')^1 + 0.33 (15a')^{-1}(16a'')^{-1}(18a')^1$
$6^2A'$	22.74		0.814	$0.89 (8a')^{-1}$
$6^2A''$	22.90		0.00371	$0.60 (14a'')^{-1}(15a')^{-1}(18a')^1 + 0.46 (14a'')^{-1}(15a')^{-1}(17a')^1$
$7^2A'$	24.00		0.06579	$0.53 (13a')^{-1}(15a')^{-1}(18a')^1 - 0.43 (13a')^{-1}(15a')^{-1}(17a')^1$
$8^2A'$	24.58		0.00329	$-0.56 (13a')^{-1}(15a')^{-1}(18a')^1 + 0.42 (14a'')^{-1}(16a'')^{-1}(18a')^1 + 0.40 (13a')^{-1}(15a')^{-1}(17a')^1$

Also shown are the measured ionization potentials—IP (exp)

<sup>a</sup> Attina et al. [1]

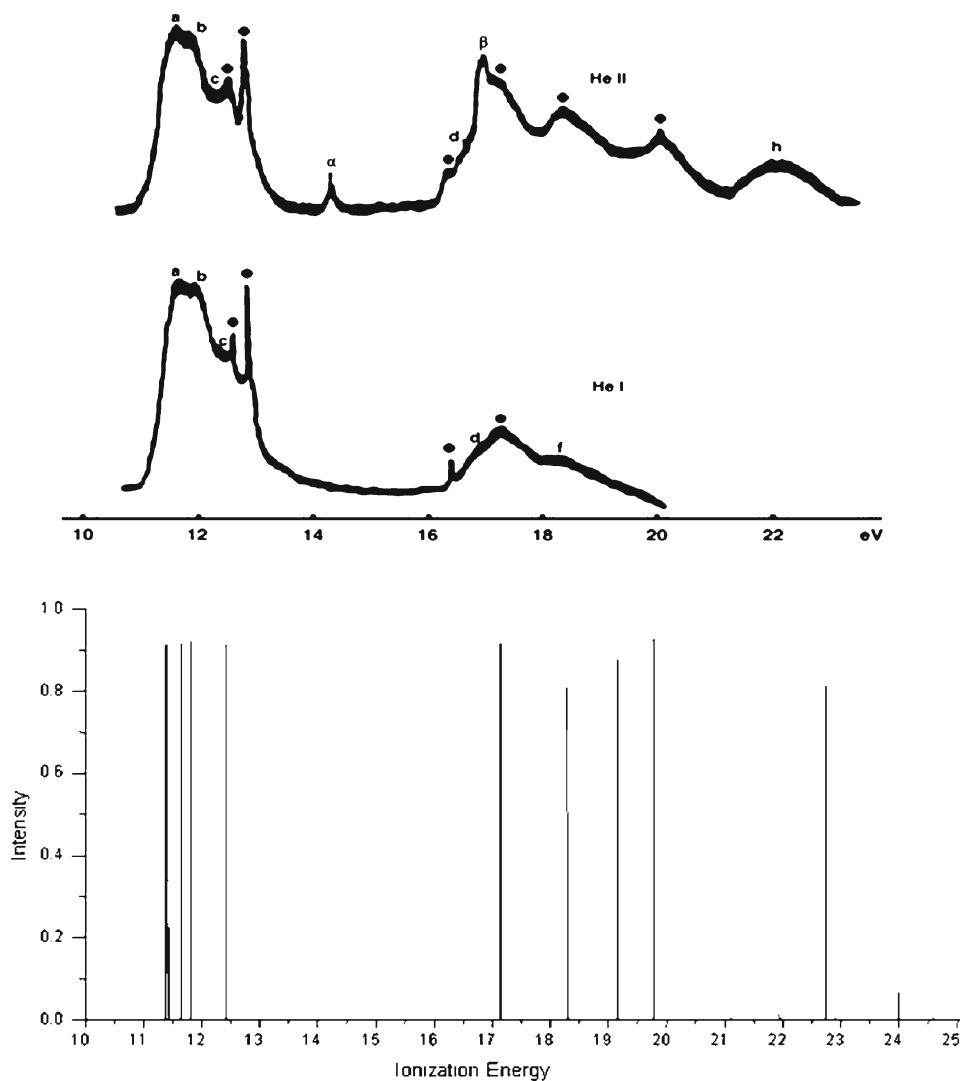
the nine states have considerable intensities in the computed spectrum and describe the experimental spectra. In particular, there is an inversion in the ordering of the first three ionized states, when compared with the expected order according to Koopmanns' theorem. The first two SAC-CI ionized states correspond to electron removals from the  $\pi$  (MO 14) and  $n\pi_{\text{NO}_2}$  (MO 16 – HOMO) orbitals, respectively. The third ionized state is the removal of an electron from the  $\sigma$  orbital (MO 15). A similar inversion, which also involves the first three ionized states, is also present in the previous *N, N*-dimethylnitramide molecule results [6].

Considering the first five ionized states, the present SAC-CI results (Table 4) and the ones from the SCF energy values according to Koopmanns' theorem (Table 1), there are considerable differences. In the most favorable case (the  $1^2A''$  state) the difference is over 1.4 eV, thereby showing the limitation of Koopmanns' theorem for the nitramide molecule even for the first ionized state, since the SAC-CI values are considerably more accurate. This accuracy of the

SAC-CI results are seen when we compare the computed ionized potential values and the experimental results. The experimental ionization potentials (IP) [1] showed in Table 4 have very good agreement with our results. This behavior is also present in the SAC-CI *N, N*-dimethylnitramide results [6]. For the nitramide molecule, the worst agreement is for the  $4^2A'$  state, which differs by 0.43 eV from the experimental value. The remaining calculated states have differences lower than 0.1 eV when compared with measured data.

The measured nitramide ionization spectrum [1], shown in Fig. 3 along with the present SAC-CI results, is detailed in Table 4. Features a, b and c, which comprise the two first bands, are described by the first four computed ionized states ( $1^2A''$ ,  $2^2A''$ ,  $1^2A'$ , and  $2^2A'$ ). The first two states remove electrons from  $\pi$  orbitals and the last two, of this group of four, from  $\sigma$  orbitals. In particular, the peak a is described by the first calculated ionized state, the b peak by the following two ionized states while the thin peak c corresponds to the

**Fig. 3** Experimental (above) [1] and theoretical SAC-CI ionization spectra. In the experimental spectrum (top panel), the peaks marked with a bullet come from  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  impurities. The peaks  $\alpha$  and  $\beta$  correspond to He self-ionizations induced by He II  $\beta$  and  $\gamma$  satellites, respectively



last ( $2^2A'$ ) of this group of states. Their relative intensities resemble the experimental peaks.

After the first four computed states, there is a gap of about 5 eV both in the experimental and the theoretical spectra. The next experimental features in the nitramide photoelectron spectra, according to Attina et al. [1], are marked by the d, e and f letters (Fig. 3, top panel). The peaks d and e are only related to one calculated state, the  $3^2A''$  ionized state, which is described by the removal of an electron from a  $\pi$  orbital. Therefore, the experimental d and e features are actually only one. The feature f, a kind of band shoulder, corresponds to three ionized states:  $3^2A'$ ,  $4^2A'$  and  $4^2A''$ . The feature h, present only in the He II spectrum (on the top of Fig. 3), is described by the  $6^2A'$  ionized state, although the contribution from the  $7^2A'$  cannot be disregarded. It is worth to note that the overall shape intensity of both spectra is theoretically well described, although this agreement is superior when the SAC-CI results are compared with the He II spectrum at the top of Fig. 3. Other ionized states, involving heavy mixing of ionized configurations, were calculated (Table 4), but have very low intensities.

#### 4 Conclusions

We computed 16 singlet and 13 triplet transitions vertical transitions employing the SAC-CI wavefunctions of the nitramide molecule,  $H_2NNO_2$ . Most of these transitions involved configuration mixing of singly excited configurations. Fourteen ionized states, including relative intensities, were obtained. The nitramide results showed strongest similarities with the *N,N*-dimethylnitramine molecule, which has also an  $N-NO_2$  bond, and was previously calculated with the same wavefunctions. The character of the nitramide transitions was theoretically established. The present results were compared with recent MS-CASPT2 calculations of the first four singlet and first three triplet transitions. In the worst case for a singlet transition, the difference between our optical oscillator strength value and the MS-CASPT2 one was 36% for the strongest transition. Agreement of our results with the corresponding MS-CASPT2 singlet and triplet transition energies is quite good, and the character of most of the computed transitions with the SAC-CI and MS-CAPT2 methods is identical, although the latter only reports one singly excited configuration for each transition while SAC-CI results entails mixture of singly excited ones.

The strongest computed transition at 6.8 eV has 0.2665 as oscillator strength and is a mixture of two  $n\pi_{NO_2} \rightarrow \pi^*$  configurations with excitations from the highest occupied molecular orbital (HOMO) to the first two virtual orbitals. The only broad band present in the gas-phase UV spectrum of nitramide was attributed to two transitions: one involving mixtures of  $n\pi_{NO_2} \rightarrow \pi^*$  configurations and the other

of  $\sigma \rightarrow \pi^*$  configurations. The triplet transitions energies could be divided into two sub-manifolds, with the first one having energies close to the first triplet transitions. The computed SAC-CI ionized states identified the available features and relative intensities of the measured photoelectron spectra, and even showed that two reported features actually correspond to only one ionized state. Our results have revealed an inversion in the ordering of the first ionized states which contradicts Koopmanns' theorem. The reported singlet, triple and ionized transitions for the nitramide molecule presented several similarities with the previously studied *N,N*-dimethylnitramide system.

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