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The Band 12 Issue in the Electron Momentum Spectra of Norbornane: A Comparison with Additional Green's Function Calculations and Ultraviolet Photoemission Measurements

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Received: December 24, 2004; In Final Form: March 21, 2005

In continuation of a recent study of the electronic structure of norbornane [*J. Chem. Phys.*, **2004**, *121*, 10525] by means of electron momentum spectroscopy (EMS), we present Green's Function calculations of the ionization spectrum of this compound at the ADC(3) level using basis sets of varying quality, along with accurate evaluations at the CCSD(T) level of the vertical (26.5 eV) and adiabatic (22.1 eV) double ionization thresholds under C_{2v} symmetry. The obtained results are compared with newly recorded ultraviolet photoemission spectra (UPS), up to binding energies of 40 eV. The theoretical predictions are entirely consistent with experiment and indicate that, in a vertical depiction of ionization, shake-up states at binding energies larger than ~ 26.5 eV tend to decay via emission of a second electron in the continuum. A band of s-type symmetry that has been previously seen at ~ 25 eV in the electron impact ionization spectra of norbornane is entirely missing in the UPS measurements and theoretical ADC(3) spectra. With regard to these results and to the time scales characterizing electron–electron interactions in EMS (10^{-17} s) as compared with that (10^{-13} s) of photon–electron interactions in UPS, and considering the p-type symmetry of the electron momentum distributions for the nearest $1b_1$ and $1b_2$ orbitals, this additional band can certainly not be due to adiabatic double ionization processes starting from the ground electronic state of norbornane, or to exceptionally strong vibronic coupling interactions between cationic states derived from ionization of the latter orbitals. It is therefore tentatively ascribed to autoionization processes via electronically excited and possibly dissociating states.

Introduction

Norbornane (C_7H_{12} , C_{2v} symmetry) is known to be an important compound in pharmaceutical research—it is useful in the therapy of cardiac infarcts or apoplectic fits¹ as well as asthma, bronchitis, and thromboses. Its outer-valence electronic structure has been early (1969) studied by Bishof et al.² and, more recently (1998), by Getzlaff and Schönhense,³ using ultraviolet [He I] photoemission spectroscopy (Figure 1a). Bieri et al. also investigated the inner valence ionization bands of this compound, up to binding energies of ~ 24 eV, by means of an He II photon beam⁴ (Figure 1b).

Of primary relevance to the present work is a recent theoretical study⁵ of the ionization spectrum of norbornane, within the framework of one-particle Green's function theory (1p-GF)^{6,7} and resorting to the so-called third-order algebraic diagrammatic construction scheme [ADC(3)]^{8–12} as well as Dunning's correlation-consistent polarized valence basis set of double- ξ quality [cc-pVDZ].¹³ These ADC(3)/cc-pVDZ calculations were performed in support of an EMS (electron momentum spectroscopy¹⁴) study of the ionization spectrum of this compound, at electron impact energies of 1.5 keV, and down to binding energies of 29 eV (Figure 1c,d). This is much beyond

the vertical shake-up and double ionization thresholds, which theory locates at ~ 22 and ~ 26 eV, respectively.⁵

The agreement between the theoretical and experimentally available [He I, He II, EMS] ionization spectra was within the usual expectations, with discrepancies on binding energies that most generally do not exceed ~ 0.2 eV, except for the $1a_2^{-1}$ ionization line at ~ 20 eV. The 1p-GF calculations overestimate the experimentally apparent ionization potential for this line by ~ 0.6 eV, which presumably reflects particularly strong geometrical relaxation effects as well as vibronic interactions. The most striking disagreement noted between theory and experiment is a strongly protruding band at ~ 25 eV in the EMS spectrum recorded at an azimuthal angle of 0° , which the ADC(3) calculations completely failed to reproduce: the ADC(3)/cc-pVDZ spectrum of norbornane does not show any dense enough set of shake-up lines that could explain the band (12) seen around 25 eV in this EMS spectrum (Figure 1d).

This failure is extremely puzzling, considering the prevalence and successes of the ADC(3) approach in studies of ionization spectra of all kind [see refs 9, 11, 15, and 16 and references therein]. This, and the fact that the momentum profiles inferred for all other bands from the angular dependence of the (e,2e) ionization intensities of norbornane are entirely consistent with the ADC(3) assignment,⁵ led us to tentatively conclude⁵ that

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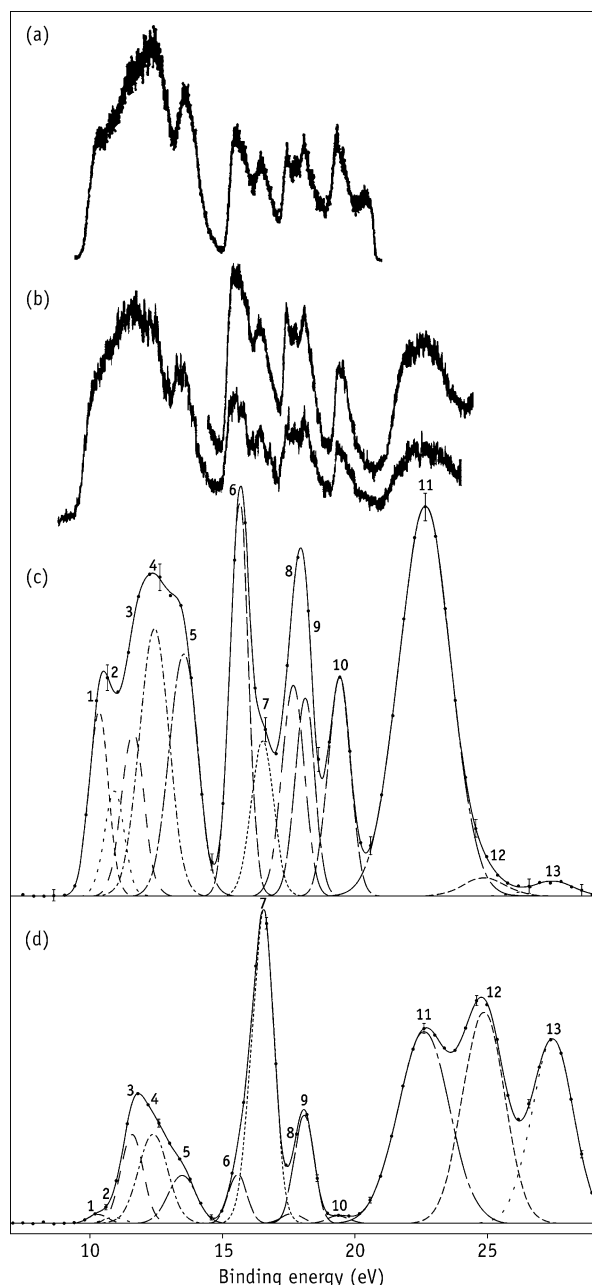


Figure 1. Experimental ionization spectra of norbornane obtained using (a) He I [3] and (b) He II [4] ultraviolet photoemission spectroscopy, or electron momentum spectroscopy at azimuthal angles of (c) $\varphi = 10^\circ$ and (d) $\varphi = 0^\circ$, respectively (adapted from ref 5).

the band at ~ 25 eV does not belong to the vertical one-electron and shake-up ionization spectrum of this compound and could relate to transitions to diffuse (Rydberg-like) electronically excited states of the cation or to auto-ionization processes. The purpose of the present work is to verify the first of these assumptions by studying the basis set dependence of the ADC(3) ionization spectrum and by comparing these new computations with further He II measurements extended up to binding energies of 40 eV.

Computations

The ADC(3) calculations, presented in ref 5, which were carried out with a cc-pVDZ basis set incorporating on total 165 contracted atomic functions, have been in the present work supplemented by calculations of the vertical ionization spectrum of norbornane performed using the standard 6-31G basis set,¹⁷

as well as Dunning's DZP+ basis set [namely, a double- ζ basis set with polarization and diffuse functions].¹⁸ The latter two basis sets include 87 and 205 basis functions, respectively. As in ref 5, the original code interfaced to the GAMESS package of programs¹⁹ has been employed to complete these 1p-GF calculations. At the SCF level, the requested convergence on each of the elements of the density matrix were fixed to 10^{-10} . With the 1p-GF/ADC(3) approach, the one-hole (1h) and shake-up two-hole-one-particle (2h-1p) ionization energies are recovered through third- and first-order in correlation, which implies accuracies of ~ 0.2 ²⁰ and ~ 0.6 eV, respectively, with a basis set approaching completeness. Constant self-energy diagrams have been computed through fourth-order in correlation, using charge-consistent²¹ one-electron densities. The spectra have been calculated up to binding energies of 29 eV, retaining all eigenvalues of the ADC(3) secular matrix with a pole strength equal to or larger than 0.005. This matrix has been diagonalized using the Block-Davidson diagonalization procedure^{22,23} in the final diagonalization step.¹¹ The assumption of frozen core electrons has been used throughout and symmetry has been exploited to the extent of the full molecular symmetry point group (C_{2v}). All ADC(3) calculations discussed in the present study are based on molecular geometries that have been optimized by means of the GAUSSIAN98²⁴ quantum chemistry package, using Dunning's basis set of triple- ζ quality²⁵ with polarized valence functions (TZVP), density functional theory (DFT) in conjunction with the nonlocal hybrid and gradient corrected Becke three-parameter Lee-Yang-Parr functional (B3LYP),^{26,27} an approach that is known to deliver excellent results for equilibrium geometries and related properties (such as vibrational frequencies).²⁸

As a guide to the eye, the identified solutions of the secular ADC(3) eigenvalue problems are displayed in Figure 2 as spike spectra and in the form of convoluted densities of states. The convolution has been performed using as a spread function a combination of a Gaussian and a Lorentzian with equal weight with a fwhm parameter of 0.6 eV and by simply scaling the line intensities according to the computed ADC(3) pole strength, neglecting thereby the varying influence of molecular orbital cross sections.

Experiment

Norbornane was purchased from Aldrich. Initial purification of the crude material was performed in vacuo to remove any volatile contaminations. Subsequently, the norbornane sample was subjected to sublimation in a Kugelrohr distillation apparatus. The fraction subliming at a heating temperature of 80–100 °C was collected. A white crystalline solid was obtained and stored under an inert atmosphere. For analysis, the ^1H NMR spectrum was recorded with a Varian Inova spectrometer at 300 MHz using a 5 mm probe and the GC-MS data were obtained with a Varian TSQ 3400 gas chromatograph and a TSQ 700 Finnigan Mat mass spectrometer. ^1H NMR (300 MHz, CDCl_3): $\delta = 2.17$ (m, 2H), 1.44 (m, 4H), 1.14 (m, 6H) ppm. Details of the recorded mass spectrum are given in Table 1, along with assignments of the main lines. It is already worth noting at this stage that, in the mass spectrum of norbornane, the intensities of lines relative to the molecular peak indicate that this compound is very prone to fragmentation into five- or six-membered rings upon ionization by electron impact at a kinetic energy of 70 eV in this case.

Photoelectron spectra were measured using the time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) ap-

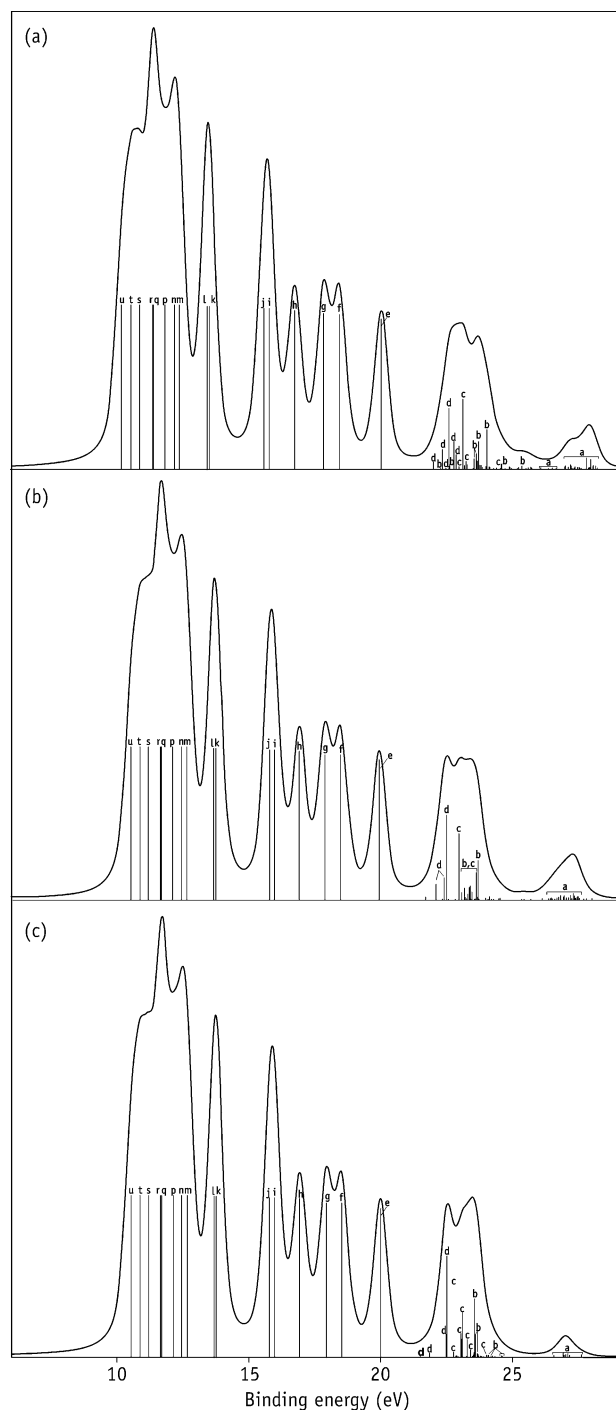


Figure 2. Theoretical ADC(3) ionization spectra of norbornane obtained using the (a) 6-31G, (b) cc-pVDZ, and (c) Dunning's DZP+ basis sets. The orbital labels are given as follows: u, 3a₂; t, 5b₂; s, 7a₁; r, 5b₁; q, 6a₁; p, 4b₂; n, 2a₂; m, 4b₁; l, 3b₂; k, 3b₁; j, 5a₁; i, 2b₁; h, 4a₁; g, 2b₂; f, 3a₁; e, 1a₂; d, 2a₁; c, 1b₂; b, 1b₁; a, 1a₁.

paratus described before.²⁹ Briefly, ionizing light from a pulsed discharge in He is wavelength-selected by a toroidal grating monochromator and refocused to intersect an effusive jet of target gas in the source of a magnetic bottle TOF electron spectrometer. The time between a light pulse and the detection of an electron at the 5.5 m distant detector is used to determine the electron energy. The energy resolution is strongly dependent on the electron energy and thus, for a given band, on the photon energy. Because individual atomic lines are selected by the monochromator, complete photoelectron spectra can be measured at any available wavelength. The spectrum of dication

states populated by double electron ejection is acquired at the same time as the simple photoelectron spectra.

Discussion of Theoretical Results

The theoretical ADC(3)/6-31G, ADC(3)/cc-pVDZ and ADC(3)/DZP+ ionization spectra of norbornane are compared in Figure 2. It is immediately apparent that all three basis sets give essentially the same distribution of ionization lines. With all three basis sets, the energy threshold for shake-up ionization processes, leading to excited configurations of the cation, is located at a binding energy of ~ 22.0 eV. At electron binding energies below that threshold, enlarging the basis set has virtually no effect on the shape and position of the convoluted bands: therefore, even a 6-31G basis set would be reliable enough to correctly assign most bands in the ionization spectrum of norbornane. These bands have already been analyzed in detail in ref 5, and this analysis will not be repeated here. Above the shake-up threshold, enlarging the basis set yields a redistribution of the ionization intensity over different sets of shake-up lines, but without very drastic changes in convoluted bands. Nonetheless, compared with ADC(3) calculations performed using the larger cc-pVDZ and DZP+ basis sets, the ADC(3)/6-31G results seem to overemphasize the dispersion of ionization intensity over shake-up lines for orbital 2a₁: with the cc-pVDZ and DZP+ basis sets, the idea of a one-electron ionization process can be partly retained for that orbital, in the form of line at a binding energy of ~ 22.4 eV with a pole strength larger than 0.5. All three basis sets indicate on the other hand that the orbital picture of ionization breaks down completely for the three innermost orbitals, namely 1b₂, 1b₁ and 1a₁. This breakdown is particularly acute for the last orbital 1a₁, and as a result only a very small fraction ($\sim 15\%$) of the 1a₁ ionization intensity could be recovered (Table 2).

Some slight but significant differences between the three simulated ionization spectra can be observed with the relative intensities of the correlation tail of orbital 1b₁, at about 25 eV, and of the innermost band at 28 eV and relating to shake-up lines originating from orbital 1a₁. It appears that both spectral features tend to disappear upon enlarging the basis set and, in particular, including diffuse functions (Figure 2c). The explanation to this observation is that enlarging the basis set implies that more shake-up states are allowed to borrow ionization intensity, thus yielding more lines with on average lower ionization intensity. The effect is more striking above the vertical double ionization threshold, which the benchmark CCSD(T) theoretical approach³⁰ locates at 26.5 eV (Table 3), in qualitatively good agreement with the results of lesser accurate approaches such as second, third and fourth order Moller–Plesset Theory (MP2, MP3, MP4SDQ). On total, a more substantial fraction of ionization intensity is lost above that energy threshold when larger basis sets are used because of the required threshold (0.005) on pole strengths. To avoid such computational artifacts, the shake-up ionization spectra should be computed by means of more sophisticated diagonalization approaches that preserve the first spectral moments, such as the block- or band-Lanczos approaches (see ref 12 and references therein). Assuming nonetheless that the limit of an infinitely complete basis set including very diffuse and continuum functions could be reached, and that the ionization intensity calculated under such a basis set could be entirely recovered for all orbitals, there is no doubt, however, that the 1a₁ band at ~ 28 eV should dilute into a very broad signal relating to a continuum of resonance and shake-off states at binding energies above ~ 26.5 eV, confirming our earlier statement⁵ that the

TABLE 1: GC-Mass Spectrum of Norbornane

peak	rel abs (%)	process	remarks
96.2	6.95	$M^+ (C_7H_{12}^+)$	
82.3	5.28	$(M^+)^* - CH_3 \rightarrow C_6H_9^+$	
81.2	77.11	$M^+ - CH_3 \rightarrow C_6H_9^+$	results possibly in six-membered closed shell cyclic species, with a double bond and a positive charge
79.2	6.82	$C_6H_9^+ - H_2 \rightarrow C_6H_7^+$	additional H-loss from the ring system
77.2	4.24	$C_6H_7^+ - H_2 \rightarrow C_6H_5^+$	additional H-loss from the ring system
68.2	65.97	$C_7H_{12}^+ - C_2H_4 \rightarrow C_5H_8^+$	bridge breaks, resulting in an opening of the ring and loss of C_2H_4
67.2	100	$C_7H_{12}^+ - C_2H_5 \rightarrow C_5H_7^+$	bridge breaks, resulting in an opening of the ring and loss of C_2H_5
66.2	11.88		additional H-loss
65.2	6.66		additional H-loss
55.2	17.73	$C_7H_{12}^+ - C_3H_5 \rightarrow C_4H_7^+$	bridge breaks, resulting in an opening of the ring and loss of C_3H_5
54.1	43.00	$C_7H_{12}^+ - C_3H_6 \rightarrow C_4H_6^+$	bridge breaks, resulting in an opening of the ring and loss of C_3H_6
53.2	15.78	$C_7H_{12}^+ - C_3H_7 \rightarrow C_4H_5^+$ or $C_5H_8^+ - CH_3 \rightarrow C_4H_5^+$	bridge breaks, resulting in an opening of the ring and loss of C_3H_7

shake-up states computed for orbital $1a_1$ are subject to decay (by ionization of a second-electron) into the continuum.

Importantly, it is clear also from Figure 2a–c that improving the basis set will not provide any satisfactory solution to the puzzling issue of band 12, at 25 eV in the (e,2e) electron impact (or EMS) ionization spectrum of norbornane (Figure 2c,d). Whereas the ionization spectrum recorded in an EMS experiment at electron impact energies of 1.5 keV, using a noncoplanar symmetric kinematics, and under an azimuthal angle of 0° by Michael Brunger and co-workers⁵ exhibits a very strongly protruding band at 25 eV, our ADC(3) spectra do not show a significantly dense and intense enough set of shake-up lines in this region. It has been conjectured⁵ that this band might partly relate to the correlation tail of orbitals $2a_1$, $1b_2$ or $1b_1$ that has not been recovered because of the finite threshold on pole strengths (see recovered fraction of ionization intensity in Table 2). However, whatever the basis set, the missing fraction of ionization intensity would be clearly far too small to fit well with that of band 12. Also, by analogy with a band-Lanczos study of the ionization spectra of *n*-alkanes,¹² the missing ionization intensity for orbital $1a_1$ is expected to be found in a very long correlation tail extending from the onset at ~ 26.9 eV up to much higher binding energies, for instance, 60 eV, and possibly beyond. Thus, the present comparison of ADC(3)/6-31G, ADC(3)/cc-pVDZ, and ADC(3)/DZP+ results confirms our earlier suggestion that band 12 in the EMS ionization spectrum of norbornane does not belong to the vertical one-electron and 2h-1p shake-up ionization spectrum of norbornane in its ground electronic state and equilibrium geometry, as described by the ADC(3) model of ionization.

Discussion of Experimental Results

The newly performed UPS measurements on norbornane (Figure 3) also fully confirm these theoretical predictions. They are fully consistent with the earlier He I and He II spectra of Getzlaff and Schönhense³ or Bieri et al.⁴ up to binding energies of 21 and 24 eV, respectively, as well as with all our ADC(3) calculations, taking into account the fact that the innermost orbital lies much above the first two-electron ionization potential. The onset of double ionization is indeed located experimentally (Figure 3) at 25 ± 0.5 eV, a value much closer to that of our most accurate [CCSD(T)/cc-pVDZ//MP2/aug-cc-pVDZ] evaluation of the vertical (~ 26.6 eV) double ionization threshold than to the value (~ 22.13 eV) obtained at the same level for the adiabatic double ionization threshold under C_{2v} symmetry (Table 3). This seems to indicate that with double ionization, geometrical relaxation effects are such in a strained species such as norbornane that the time required for a complete geometrical relaxation of the dication strongly exceeds the time scale characterizing UPS upon a 40 eV photon beam ($\sim 10^{-13}$ s, see

later), and rules out therefore the scenario that band 12 in the EMS record of Figures 1c,d would relate to transitions from the electronic ground state of norbornane in equilibrium geometry to the lowest adiabatically relaxed singlet or triplet doubly ionized state. Note also that the experimentally observed shake-off band shows a slight extremum at ~ 29 eV, as a reminiscence of the densest sets of the vertical shake-up states found for the $1a_1$ orbital at the ADC(3) level.

The measurements performed using wavelengths of 304 and 256 Å show also some very long and weak signal extending between 24 and 27 eV, which should be related to the correlation tail of band 11 and, more specifically, of orbitals $1b_2$ and $1b_1$. This tail is more strongly apparent in the ADC(3)/6-31G spectrum of Figure 2a and tends to disappear in the ADC(3) spectra obtained with a larger basis set, as a result of enhanced shake-up fragmentations and the limitation of the search to the solutions of the ADC(3) secular equation to lines with a pole strength larger than 0.005. Because it is a well-established principle that shake-up lines originating from the same orbital have relative intensities proportional to their pole strength, this tail, and the missing ionization intensity for orbitals $1b_2$ and $1b_1$ in the ADC(3) simulations of Figure 2, are far too weak to be related to such an intense and striking feature as band 12 in the EMS measurement of Figure 1d. Also, it is worth reminding that the momentum distribution inferred from band 12 is of s-type and is therefore completely incompatible with the p-type

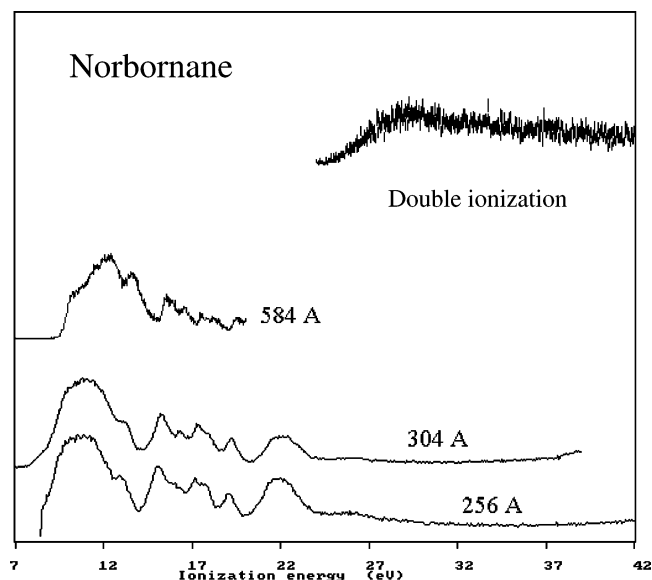


Figure 3. Newly recorded ultraviolet photoemission [He I, He II] spectra at incident photon energies of 21.25 eV ($\lambda = 584$ Å), 40.82 eV ($\lambda = 304$ Å) and 48.47 eV ($\lambda = 256$ Å). At the right top, the experimental double ionization spectrum is given.

TABLE 2: Present ADC(3) and Experimental UPS Results for the Ionization Spectrum of Norbornane^a

Table 2. Calculated T_e (eV) and experimental T_e (eV) for the dominant spectrum of two boron												
symbol	level	HF/cc-pVDZ	ADC(3)/6-31G		ADC(3)/cc-pVDZ		ADC(3)/DZP+		experimental			
									He I ³	He II 304 Å	He II 256 Å	EMS ⁵
u	3a ₂	11.328	10.183	(0.917)	10.513	(0.908)	10.515	(0.908)	~10.3	~11.2	~11.2	10.3 [1]
t	5b ₂	11.641	10.544	(0.917)	10.863	(0.908)	10.852	(0.908)				10.9 [2]
s	7a ₁	12.006	10.865	(0.916)	11.189	(0.906)	11.178	(0.907)	~10.9			10.9 [2]
r	5b ₁	12.531	11.363	(0.914)	11.657	(0.905)	11.640	(0.905)	~11.6			11.6 [3]
q	6a ₁	12.607	11.372	(0.915)	11.670	(0.906)	11.670	(0.906)				11.6 [3]
p	4b ₂	13.108	11.816	(0.914)	12.102	(0.905)	12.111	(0.905)				12.4 [4]
n	2a ₂	13.384	12.178	(0.915)	12.445	(0.905)	12.445	(0.906)	~12.4			12.4 [4]
m	4b ₁	13.634	12.355	(0.914)	12.645	(0.904)	12.643	(0.905)				12.4 [4]
l	3b ₂	14.734	13.426	(0.910)	13.657	(0.901)	13.657	(0.901)	~13.6	~13.3 (j)	~13.3	13.5 [5]
k	3b ₁	14.831	13.479	(0.911)	13.736	(0.901)	13.735	(0.902)				13.5 [5]
j	5a ₁	16.999	15.569	(0.901)	15.757	(0.892)	15.752	(0.893)	~15.6	~15.6	~15.5	15.6 [6]
i	2b ₁	17.232	15.764	(0.898)	15.948	(0.890)	15.936	(0.890)				15.6 [6]
h	4a ₁	18.360	16.722	(0.890)	16.897	(0.882)	16.887	(0.883)	~16.5	~16.6	~16.4	16.5 [7]
g	2b ₂	19.772	17.814	(0.872)	17.866	(0.863)	17.877	(0.864)	~17.7	~17.6	~17.5	17.65 [8]
f	3a ₁	20.500	18.423	(0.865)	18.473	(0.856)	18.475	(0.858)	~18.1		~18.0 (j)	18.1 [9]
e	1a ₂	22.328	19.999	(0.838)	19.926	(0.832)	19.943	(0.833)	~19.4	~19.4	~19.4	19.4 [10]
d	2a ₁	25.542	21.976	(0.042) (c)	22.088	(0.094) (a)	21.788	(0.025) (e)		~22.2	~22.1	~22.6 [11]
			22.320	(0.112)	22.389	(0.132) (b)	22.413	(0.135) (f)				
			22.565	(0.341)	22.484	(0.507)	22.443	(0.571)				
			22.758	(0.157)								
			22.834	(0.078)								
				(0.789) (+)		(0.764) (+)		(0.731) (+)				
				(0.390)	22.951	(0.392)	22.701	(0.031)				
			23.213	(0.046)	23.053	(0.044)	22.980	(0.137)				
			23.258	(0.025) (d)	23.162	(0.071)	23.022	(0.032)				
			23.528	(0.025)	23.345	(0.077)	23.029	(0.250)				
c	1b ₂	26.570	23.626	(0.050)	23.448	(0.037)	23.219	(0.100)				
			23.683	(0.050)	24.108	(0.020)	23.349	(0.044)				
			23.744	(0.023)			23.466	(0.031)				
			23.796	(0.023)								
			24.533	(0.029)								
				(0.720) (+)		(0.725) (+)		(0.702) (+)				
			23.156	(0.023)	23.167	(0.021)	23.500	(0.031)				
			23.530	(0.059)	23.287	(0.036)	23.505	(0.328)				
			23.611	(0.087)	23.378	(0.084)	23.536	(0.129)				
			23.689	(0.154)	23.444	(0.049)	23.602	(0.025)				
b	1b ₁	27.067	24.012	(0.222)	23.597	(0.165)	23.641	(0.022)				
			24.559	(0.031)	23.663	(0.236)						
				(0.737) (+)		(0.697) (+)		(0.662) (+)				
			26.991	(0.020)	26.804	(0.028)	26.504	(0.015)				
			27.18	(0.028)	26.930	(0.027)	26.866	(0.029)				
			27.773	(0.064)	27.183	(0.025)	26.891	(0.014)				
			27.933	(0.021)	27.279	(0.038)	26.899	(0.011)				
			28.012	(0.023)	27.331	(0.026)	26.956	(0.018)				
			28.037	(0.021)	27.432	(0.020)	27.032	(0.022)				
			28.127	(0.021)			27.093	(0.016)				
a	1a ₁ (g)	31.532					27.531	(0.020)				
				(0.452) (+)		(0.481) (+)		(0.145) (+)				

TABLE 3: Determination of the Vertical and Adiabatic Double Ionization Potentials (VDIP and ADIP, Respectively) of Norbornane Associated with the Lowest Singlet (S) and Triplet (T) States of the Dication^a

theoretical level	VDIP (eV) ^b		VDIP (eV) ^c		ADIP (eV) ^d	
	S	T	S	T	S	T
HF/cc-pVDZ	27.246	26.073	27.168	26.018	24.334	24.969
MP2/cc-pVDZ	26.015	26.524	25.931	26.460	24.714	26.739
MP3/cc-pVDZ	26.943	26.834	26.867	26.775	23.662	25.146
MP4/cc-pVDZ	27.063	26.830	26.987	26.772	23.481	24.891
CCSD/cc-pVDZ	27.033	26.728	26.959	26.672	23.472	24.871
CCSD(T)/cc-pVDZ	26.571	26.475	26.496	26.419	22.131	23.715
MP2/aug-cc-pVDZ	26.052	26.587	25.968	26.524	23.507	25.561

^a Results were obtained by means of single-point calculations upon B3LYP/TZVP or MP2/aug-cc-pVDZ geometries, within the constraint of a C_{2v} point group. ^b Single-point calculations, using the B3LYP/TZVP geometry of the neutral in its singlet ground state. ^c Single-point calculations, using the MP2/aug-cc-pVDZ geometry of the neutral in its singlet ground state. ^d From the results of single-point calculations upon MP2/aug-cc-pVDZ geometries for the neutral and adiabatically relaxed doubly ionized forms of norbornane.

shake-up and/or shake-off states derived from the innermost C_{2s} orbital, $1a_1$, and because molecular orbitals having similar atomic compositions normally display comparable UPS cross sections, these bands would both have intensities in the same range as those seen for the other inner-valence orbitals encompassed in band 11 ($1b_1$, $1b_2$ and $2a_1$).

It is worth noting that very significant discrepancies, up to 4 eV, have already been noted previously between the appearance potentials for double ionization in electron and photon impact experiment.^{41,42} The reasons for these discrepancies can be instrumental, i.e., due to inherent differences in the determination of the onset of the appearance potentials for double ionization, and (or) related to intrinsic molecular properties and different behaviors under electron and photon impact. Wannier theory⁴³ and its extension by Geltman⁴⁴ indicate that, for an electron as compared with photon impact, the (total) cross section for direct double ionization should rise less steeply, at threshold, as a function of the energy of the impinging particle. Higher appearance potentials for double ionization processes are thus normally expected in electron impact experiments, as compared with photon impact, and it seems therefore unlikely that the presence of an additional band at 25 eV in the EMS measurements on norbornane as compared with the newly presented UPS ones can be explained on such grounds. In the experimental setup employed for these EMS experiments, the impinging electron has a kinetic energy of 1.5 keV, which also rules out the possibility of a breakdown of the Born (sudden, or knocked-out) approximation, and thus the excitation of optically forbidden triplet states because of electron exchange in the target molecule (this energy is much above the 200 eV limit beyond which the Born approximation is usually considered to be valid).

The duration of interaction of a photon with an energy in the 20–40 eV range and incident on a molecule of a few angstroms in dimension is much longer than for an electron with an energy of 1.5 keV. This interaction time depends on the specific physical processes involved in energy transfer in each case. The photoionization process requires typically about 500 cycles of the radiation field (according to ref 41) to fully manifest its harmonic character during the perturbation time. For a photon of 40 eV, this corresponds to an interaction time of the order of 0.05 ps. For an electron, the duration of interaction with the molecule depends on the distance over which direct momentum transfer can occur between the incident electron and the molecular electrons. This range, limited to the close collision

region, can be taken to be about 3 Å. Because the velocity of a 1.5 keV electron is about 2.28×10^9 cm s⁻¹, it will traverse 3 Å in about 0.01 fs. Thus, the effective interaction time of a molecule with a 1.5 keV electron should be about 4 orders of magnitudes smaller than with a 40 eV photon. An electron that collides with a molecular target in the EMS experiment with an energy of ~1.5 keV has a collision time of $\sim 10^{-17}$ s, whereas with UPS the interaction time is around 10^{-13} s. Ultraviolet photon ionization tends therefore to be an adiabatic process, whereas with EMS, ionization remains normally nonadiabatic as far as geometry relaxation and nuclear motions are concerned. From a time scale viewpoint, the presence of an additional peak at 25 eV in EMS as compared with UPS seems therefore highly paradoxical. Because this band is clearly missing in UPS and has a momentum distribution very similar to that of orbital $1a_1$, band 12 in Figures 1c,d might therefore be indicative of ultrafast and unidentified electronic or nuclear dynamical processes, at time scales between 0.1 ps and 0.01 fs, that are initiated by double ionization of the norbornane compound. The most attractive scenario is an indirect ionization process in which highly electronically superexcited singlet and triplet states of the neutral target molecule are initially formed, followed by single-electron, shake-up or double autoionization, with possibly as ultimate consequence a charge separation or covalent molecular fragmentation of the carbon cage. Assuming that the autoionization scenario is valid, the latter complications are quite likely to occur with regards to the extent of cyclic strains within a cage structure such as norbornane, and which single and almost double ionization events should clearly intensify. It is worth noting that single-electron ionization processes following molecular dissociation events are known to result into additional bands at fixed electron kinetic energies and relatively high apparent electron binding energies in [Penning] ionization experiments upon collision with metastable excited atoms (see ref 45 and references therein). Note also that, if autoionization processes would indeed occur upon molecular dissociation, the “final” states effectively observed by means of EMS or UPS would clearly be completely different, considering the very different time scales of the two spectroscopies.

Conclusions

In extension to a recent study of the electronic structure of norbornane using electron momentum spectroscopy in conjunction with calculations of orbital momentum distributions by means of density functional theory as well as Green's function calculations of the ionization spectrum, we made use again of the ADC(3) approach to compare spectra obtained using basis sets of improving quality (6-31G, cc-pVDZ, DZP+) with newly performed high-resolution He I and He II measurements, up to binding energies of ~40 eV. The present work fully confirms the former suggestion⁵ that a band observed at 25 eV in the ($e,2e$) ionization spectrum of norbornane upon impact with a 1.5 keV electron does not belong to the vertical one-electron and shake-up ionization spectrum of this compound in its ground state and equilibrium geometry. Furthermore, extrapolating to the asymptotic limit the dependence of the computed sets of shake-up lines on the basis set also show that, in a vertical depiction, this band cannot relate to vertical double ionization processes. This finding is in line with further benchmark quantum mechanical results for the vertical and adiabatic double ionization thresholds under C_{2v} symmetry, which are located at 26.5 and 22.1 eV, and with newly presented ultraviolet photoelectron measurements, in which this band is entirely missing (in UPS, the onset of double ionization is located at

~25 eV, and the extremum of intensities in shake-off bands is not reached before 29 eV). Considerations on relative time scales, on the extent of geometrical relaxation effects, as well as on the s-type symmetry characterizing the momentum distributions inferred in EMS from the innermost valence bands rule out the scenarios that band 12 is the result of exceptionally strong vibronic coupling interactions between states originating from ionization of the 1b₁ and 1b₂ orbitals, or of double adiabatic ionization processes starting from the ground-state electronic wave function of norbornane in its equilibrium geometry. It would thus be worth redoing further EMS measurements on norbornane at varying energies for the incoming electron, to test the remaining hypothesis⁵ of single or double autoionization processes via electronically highly excited and possibly dissociating states.⁴⁵ The absence of such a spectral feature in ultraviolet photoemission spectroscopy suggests indeed that the band seen at 25 eV in the (e,2e) electron impact ionization spectra of norbornane⁵ relates to ultrafast autoionization and/or coulomb fragmentation processes, at time scales between 10⁻¹⁴ and 10⁻¹⁷ s, that are induced specifically by double ionization. Measurements of electron energy loss spectra at large deflection angles, and of mass spectra at varying electron kinetic energies, would for this reason also be most welcome. On the side of theory, detailed quantum chemical investigations of the potential energy surfaces of norbornane²⁺, both in its singlet and triplet forms, are necessary for elucidating the present enigma, and will be presented in a separate study.⁴⁶

Acknowledgments. This work was supported by the Bijzonder Onderzoeks Fonds (BOF) of the Limburgs Universitair Centrum and the Fonds voor Wetenschappelijk Onderzoek Vlaanderen (FWO), namely the Flemish branch of the National Scientific Foundation of Belgium. M.S.D. and S.K. are indebted to Prof. M. Takahashi (Institute for Molecular Science, Okazaki, Japan) and Dr. M. Vos (Atomic and Molecular Physics Laboratories, Australian National University, Canberra, Australia) for useful discussions on electron momentum spectroscopy.

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