J. Am. Chem. Soc. 1994, 116, 5927-5936

Theoretical and Experimental Determination of the Electronic Spectrum of Norbornadiene

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Received December 10, 1993. Revised Manuscript Received April 4, 1994[●]

Abstract: The electronic spectrum of the nonplanar, indirectly conjugated molecule norbornadiene has been studied theoretically, using multiconfigurational second-order perturbation theory (CASPT2) with extended ANO-type basis sets, and experimentally, using optical absorption and polarization-selected two-photon resonant-enhanced multiphoton ionization (REMPI) spectroscopies. The calculations comprise five valence excited states and the 3s, 3p, and 3d members of the Rydberg series converging on the first two ionizations. The two lowest triplet states have also been studied. The experiments enabled definitive assignments to be made for four Rydberg transitions and three valence transitions. The computed excitation energies were found to be within 0.2 eV of the experimental energies for correctly correlated transitions; the computed oscillator strengths were in good relative agreement with their experimental values. Comparisons are made between this and other theoretical calculations and also between the electronic spectra of norbornadiene, *cis*-butadiene, and cyclopentadiene.

1. Introduction

Norbornadiene, bicyclo[2.2.1]hepta-2,5-diene, is a formally unconjugated, strained, nonplanar diene.[1] It is the next and most complicated molecule in the series *cis*-butadiene, cyclopentadiene, norbornadiene. The first two members of this series have been previously studied, and agreement was observed between the calculated and experimental spectra of the second.[2,3] For norbornadiene, despite considerable effort devoted to the study of its electronic spectrum,[4-15] less information is available than for cyclopentadiene, and the results of calculations performed until now are not in good agreement with those of experiment. Calculations on norbornadiene are more difficult, since both indirect conjugation and π,σ interaction must be considered. Another reason is the complexity of the experimental spectrum. As the computational problems are common in complex molecules, up to and including buckminsterfullerene,[16] a full theoretical description of the spectrum of norbornadiene is of value both in itself and as an assessment of the ability of current computational methods to successfully treat complex molecules. The present contribution is such a combined *ab initio* and experimental analysis of the main electronic transitions of norbornadiene in the energy region below 8.0 eV.

For the qualitative description of the transitions of norbornadiene it is helpful to consider first the interaction of the formally unconjugated ethylenic moieties. The interaction of the degenerate bonding, π_b, and antibonding, π_a, molecular orbitals (MOs) of the two ethylenic units results in the following four MOs:[17] $\pi_1 = \pi_b + \pi_b$, $\pi_2 = \pi_b - \pi_b$, $\pi_3 = \pi_a + \pi_a$, and $\pi_4 = \pi_a - \pi_a$. Hoffmann and co-workers[9] have shown two distinct symmetry-controlled mechanisms for interaction of π systems. When the geometry of a molecule permits direct spatial overlap of the orbitals on each of the chromophores, the interaction is of the through-space (TS) type. In order of increasing energy the level ordering is π_1, π_2, π_3, and π_4, the so-called normal ordering. The through-bond (TB) or hyperconjugative interaction leads to destabilization of the in-phase with respect to the out-of-phase combinations of the two ethylenic π MOs, yielding the reverse level ordering, π_2, π_1, π_4, and π_3. The model for dominant TS interaction of unconjugated double bonds is norbornadiene with the normal orbital ordering, $a_1(\pi_1)$, $b_1(\pi_2)$, $b_2(\pi_3)$, and $a_2(\pi_4)$ in the C_{2v} point group of norbornadiene. It might be worth noting that the same normal level ordering is found in conjugated dienes like *cis*-1,3-butadiene and cyclic dienes like cyclopentadiene, $b_1(\pi_1)$, $a_2(\pi_2)$, $b_1(\pi_3)$, and $a_2(\pi_4)$, although the symmetries of the different π orbitals of the conjugated dienes differ from those of norbornadiene because of the different orientation of the C_2 axis. The separation between the occupied π-derived orbitals of norbornadiene resulting from this through-space interaction was observed to be 0.95 eV by Rydberg spectroscopy,[12] close to the photoelectron value,[18] 0.85 eV, and appreciably less than is observed for fully conjugated cyclopentadiene, 2.16 eV.[19] The orbital splitting between the

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[●] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

(1) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356.

(2) (a) Serrano-Andrés, L.; Merchán, M.; Nebot-Gil, I.; Roos, B. O.; Fülscher, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 6184. (b) Serrano-Andrés, L.; Merchán, M.; Fülscher, M. P.; Roos, B. O. *Chem. Phys. Lett.* **1993**, *211*, 125.

(3) (a) McDiarmid, R.; Sabljic, A. *J. Phys. Chem.* **1991**, *95*, 6455. Sabljic, A.; McDiarmid, R.; Gedanken, A. *J. Phys. Chem.* **1992**, *96*, 2442. (b) McDiarmid, R.; Sabljic, A. *J. Chem. Phys.* **1990**, *93*, 3850.

(4) Wilcox, C. F., Jr.; Winstein, S.; McMillan, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5450.

(5) Hermann, R. B. *J. Org. Chem.* **1962**, *27*, 441.

(6) Roquitte, B. C. *J. Phys. Chem.* **1965**, *69*, 2475.

(7) Yamakawa, M.; Kubota, T. *Shionogi Kenkyusho Nempo* **1965**, *15*, 109. *Chem. Abstr.* **1966**, *64*, 12053.

(8) (a) Robin, M. B.; Kuebler, N. A. *J. Chem. Phys.* **1966**, *44*, 2664. (b) Robin, M. B.; Kuebler, N. A. *J. Mol. Spectrosc.* **1970**, *33*, 274.

(9) (a) Hoffmann, R.; Heilbronner, E.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 706. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(10) Frueholz, R. P.; Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *J. Chem. Phys.* **1979**, *70*, 1986.

(11) Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 5749.

(12) Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1981**, *75*, 87.

(13) Galasso, V. *Chem. Phys.* **1991**, *153*, 13.

(14) Zgierski, M. Z.; Zerbetto, F. *J. Chem. Phys.* **1993**, *98*, 14.

(15) Allan, M. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 219.

(16) Haddon, R. C. *Science* **1993**, *261*, 1545.

(17) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 121.

(18) Bischof, V. P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(19) Derrick, P. J.; Asbrink, L.; Edqvist, O.; Jonsson, B.-Ö.; Lindholm, E. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *6*, 203.

0002-7863/94/1516-5927$04.50/0

vacant antibonding orbitals of norbornadiene was found[12,15,20] to be 1.56 eV by electron-transmission spectroscopy,[15] greater than the orbital splitting of the occupied levels but again smaller than the 2.11 eV observed for cyclopentadiene.[21]

On the basis of the structure, close spacing of the π-derived MOs, and our own experience with related systems[2,22] the spectrum of norbornadiene can be roughly predicted. There will be five low-lying valence excited states in norbornadiene to which transitions from the ground state can occur. The one-electron promotions $\pi_2 \rightarrow \pi_3$ and $\pi_1 \rightarrow \pi_4$ give rise to two states of A_2 symmetry, while the one-electron promotions $\pi_1 \rightarrow \pi_3$ and $\pi_2 \rightarrow \pi_4$ result in two states of B_2 symmetry. The latter are quasi-degenerate and interact to form B_2^- and B_2^+ states. The minus state has the lower energy and low intensity; the plus state is pushed up and carries most of the intensity. So far this resembles that predicted for cyclopentadiene except that in the latter the first pair of states are of B_2 symmetry and the second pair of A_1 symmetry. In both molecules there is an additional low-lying state of A_1 symmetry formed from two-electron promotions, mainly $(b_1)^2 \rightarrow (b_2)^2$. In cyclopentadiene this third state of A_1 symmetry can interact with the other two A_1 states and further alter their energies. In cyclopentadiene it has, in fact, been argued[23] and this interaction forces the lowest A_1 state below the lower B_2 state, a finding at variance with our recent *ab initio* results on cyclopentadiene.[2] As no such interaction is possible in norbornadiene, the comparison of a comparable pair of *ab initio* and semiempirical calculations may aid in resolving this conflict. In addition to singlet states, triplet excited valence A_2 and B_2 states are expected. They are predicted to lie somewhat lower in energy than their corresponding singlets. Rydberg states, states formed by promotions from the occupied orbitals to large radius atomic-like orbitals, are expected to be interleaved among the valence excited states of norbornadiene. Because of the closeness of the energies of the b_1 and a_1 π orbitals in norbornadiene, Rydberg states arising from excitations out of both these orbitals are predicted to be close in energy.

Unfortunately, the experimental spectrum of norbornadiene is expected to be difficult to interpret for additional reasons. The photoelectron spectrum of norbornadiene[24] has been shown to contain a long vibrational progression with an origin–peak energy displacement of around 0.3 eV. Similar broad structured bands are, therefore, anticipated for at least the Rydberg transitions, which, given the small spacing anticipated between different electronic transitions, will probably overlap. Both the optical[8] and lower resolution electron-impact spectra of norbornadiene[12] support this prediction as do optical absorption[4,6–8] and circular dichroism (CD)[11] measurements. Many broad singlet → singlet transitions were observed in the 4.5–9 eV range in an electron energy loss investigation of norbornadiene. They were assigned as transitions to four valence states, two dipole-forbidden transitions at 5.25 and 7.50 eV, two dipole-allowed transitions at 5.95 and 6.65 eV, and nine Rydberg transitions on the basis of their energies and electron-scattering properties.[12] Two low-lying singlet → triplet transitions were detected by Frueholz *et al.*,[10] with estimated intensity maxima at 3.4 and 3.9 eV. They have more recently been confirmed by Allan,[15] who reported the vibrationally resolved energy loss spectra of norbornadiene in this region. Evidence of higher triplet states was also presented in the latter investigation. Assignments of the first optically allowed "transition" as the composite of a structured Rydberg transition to the first ionization limit superimposed on a diffuse valence transition were suggested on the basis of the sensitivity of the structured transition to environment,[8] its quantum defect, and its presumed series limit.[10,12,15] Some two-photon resonant-enhanced multiphoton ionization (REMPI) spectroscopic data have also been presented and interpreted.[24] On the basis of the preliminary analysis the most intense feature of the spectrum, the band with an intensity maximum at 6.65 eV, is predicted to correspond to the transition energy to the second optically active valence-excited state, hopefully the B_2^+ state.

Norbornadiene has been theoretically studied with several semiempirical approaches.[4,5,9,14] They have not been able to provide a complete and consistent picture of the spectrum. To our knowledge, there exist only two previous *ab initio* calculations on this molecule, one employing the random phase approximation (RPA)[11,13] and the other the configuration interaction singles (CIS) procedure.[14] In the latter the states are not identified by type, which creates ambiguities in attempts to correlate the results of this calculation with either the experimental transitions or those calculated here. Neither of these studies were able to yield an acceptable interpretation of the spectrum.

The current investigation encompasses both a theoretical and an experimental investigation of the excited electronic states of norbornadiene. The theoretical study uses the complete active space (CAS) SCF approximation[25] in combination with a recently developed multiconfigurational second-order perturbation approach, the CASPT2 method.[26] Its validity in calculating the differential correlation effects on excitation energies has been demonstrated in a number of earlier applications.[2,22,27–29] We have recently presented results from the CASPT2 study of the electronic spectra of polyenes[22] (ethene, butadiene, hexatriene, and octatetraene) and heterocyclic pentadienes[2] (cyclopentadiene, pyrrole, furan, and thiophene). The resulting transition energies and oscillator strengths are in agreement with the experimental results.[3] As indicated above, we seek here to determine the reliability of the methodology for a rigid and strained system, where σ–π separability does not occur.

The experimental investigation is a combined optical absorption and polarization-selected (2+1) resonant-enhanced multiphoton ionization (REMPI) spectroscopic study of the spectrum of static and jet-cooled samples of norbornadiene. The optical spectrum was remeasured with better resolution. The REMPI spectrum was measured both to search for optically forbidden transitions and to identify the polarizations of the observed transitions so definitive assignments could be made.

The paper is organized as follows. Details of the theoretical approach and the calculations are described in the next section. Details of the experimental measurements are presented after that. Next, the experimental results and analysis are presented, followed by the theoretical results, analysis, comparisons to previous theoretical studies, and comparisons to experimental data. Our conclusions concerning the quality of the calculation, the quality of other calculations, and a discussion of the features common to related dienyl systems constitute the next-to-last section of the paper. A summary is last.

2. Theoretical Methods and Computational Details

2A. Geometry and basis sets. The ground-state geometry determined in gas phase by electron diffraction[1] was employed

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(20) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *Chem. Phys. Lett.* **1976**, *42*, 227.

(21) Staley, S. W.; Bjorke, M. D.; Giordan, J. C.; McMillan, M. R.; Moore, J. *J. Am. Chem. Soc.* **1981**, *103*, 7057.

(22) (a) Serrano-Andrés, L.; Merchán, M.; Nebot-Gil, I.; Lindh, R.; Roos, B. O. *J. Chem. Phys.* **1993**, *98*, 3151. (b) Serrano-Andrés, L.; Roos, B. O.; Merchán, M. *Theor. Chim. Acta*, in press. (c) Serrano-Andrés, L.; Lindh, R.; Roos, B. O.; Merchán, M. *J. Phys. Chem.* **1993**, *97*, 9360.

(23) Zgierski, M. Z.; Zerbetto, F. *J. Chem. Phys.* **1993**, *99*, 3721.

(24) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: Orlando, 1985; Vol. III, p 329.

(25) For a review of the CASSCF method see: B. O. Roos, in *Ab Initio Methods in Quantum Chem.-II*; Lawley, K. P., Ed.; J. Wiley & Sons Ltd.: New York, 1987; p 399.

(26) (a) Andersson, K.; Malmqvist, P.-A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(27) Roos, B. O.; Andersson, K.; Fülscher, M. P. *Chem. Phys. Lett.* **1992**, *192*, 5.

(28) Fülscher, M. P.; Andersson, K.; Roos, B. O. *J. Phys. Chem.* **1992**, *96*, 9204.

(29) Fülscher, M. P.; Roos, B. O. *Theor. Chim. Acta* **1994**, *87*, 403.

in the calculation. Calculations were carried out within C_{2v} symmetry, placing the CH_2 fragment in the *xz* plane with the *z* axis bisecting the HCH angle.

Generally contracted basis sets of atomic natural orbital (ANO) type[30] are used. They have been obtained[31] from (14s9p4d) and (8s4p) primitive sets for carbon and hydrogen, respectively. The contraction C[4s3p1d]/H[2s1p] was employed, which was shown in previous studies[2,22,27-29] to be flexible enough for a proper description of the valence excited states. The inclusion of diffuse functions is required in order to treat in an adequate way the 3s, 3p, and 3d Rydberg states described by excitations out of the highest occupied molecular orbital (HOMO) b_1 and (HOMO-1)a_1. A procedure to obtain optimal Rydberg functions for a given molecule has been recently developed.[32] It has the aim of introducing a precise but limited set of Rydberg functions well separated from the ordinary basis set used to describe the valence orbitals. This is important in the CASPT2 procedure in order to minimize the occurrence of intruder states caused by the presence of a large number of diffuse functions. Using this procedure,[32] a final set of s-, p-, and d-type diffuse functions was built for norbornadiene. The original basis set was supplemented with a 1s1p1d set of Rydberg functions (contracted from a set of 8s8p8d primitives), which was placed in the averaged charge centroid of the $^2B_1$ and $^2A_1$ states of the norbornadiene cation. A total of 175 basis functions were used in the calculations.

2B. CASSCF and CASSI Calculations. In the current investigation multiconfigurational wave functions were initially determined at the CASSCF level of approximation.[25] The carbon 1s electrons were kept frozen in the form determined by the ground-state SCF wave function. The total SCF energy for the ground state ($^1A_1$) of norbornadiene was calculated to be -269.726 014 au. The four π-related electrons were chosen to be active and the remainder inactive. The choice of an active space is determined by the type of excited state to be studied. For norbornadiene these will be valence excited states and excitations from the HOMO and HOMO-1 to the 3s, 3p, and 3d Rydberg orbitals. In order to limit its size, different active spaces are used for different types of excited states. We shall label the active spaces (*klmn*), where the indices give the number of orbitals of each of the four irreducible representations of the C_{2v} point in the order a_1, b_1, b_2, and a_2. The π-derived valence active space is thus denoted by (1111). It has been used in the computation of the low-lying $^3A_2$ and $^3B_2$ states. For the study of the singlet excited states the active space was extended to include the corresponding Rydberg orbitals of symmetry a_1 (3s, $3p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$), b_1 ($3p_x$, $3d_{xz}$), b_2 ($3p_y$, $3d_{yz}$), and a_2 ($3d_{xy}$), as appropriate. In addition, extra orbitals were included in the active space of each symmetry to study the spectral consequences of excitations to these orbitals. These involve mainly π–σ^* type transitions. In some cases, extra orbitals were also added to the active space to minimize the effect of intruder states in the CASPT2 calculations. As long as the active space is not so small that intruder states appear in the CASPT2, the results have been shown not to be very sensitive to further addition of orbitals in the active space.[2,22,27-29] The active spaces used and the type of states computed are summarized in Table 1.

In later tables, and in the Discussion, the energy of each excited state is referenced to a ground-state energy computed with the same active space. The molecular orbitals for the excited states were obtained from average CASSCF calculations, where the averaging includes all states of interest of a given symmetry. The number of states included in the state average CASSCF calculations is listed in Table 1 together with the number of configurations in the CASSCF wave function, which is employed as the reference function in the second-order perturbation treatment of each state.

Table 1: CASSCF Wave Functions (Four Active Electrons) Employed to Compute the Valence and Rydberg Excited States of Norbornadiene

wave function[a]	states	no. conf[b]	N_{states}[c]
CASSCF(1111)	$^3A_2(T_1)$	4	1
	$^3B_2(T_2)$	4	1
CASSCF(1411)	$^1A_1(b_1 \rightarrow 3p, 3d)$	61	6
	$^1B_1(a_1 \rightarrow 3p, 3d)$	45	4
CASSCF(7111)	$^1A_1(V_5; a_1 \rightarrow 3s, 3p, 3d)$	297	7
	$^1B_1(b_1 \rightarrow 3s, 3p, 3d)$	176	6
CASSCF(1143)	$^1B_2(V_2; V_3; b_1 \rightarrow 3d; a_1 \rightarrow 3p, 3d)$	119	6
	$^1A_2(V_1; V_4; b_1 \rightarrow 3p, 3d; a_1 \rightarrow 3d)$	119	6

[a] Within parentheses the number of active orbitals of symmetry a_1, b_1, b_2, and a_2, respectively. [b] Number of configurations in the CASSCF wave function. [c] States included in the state average CASSCF calculation.

The CASSCF state interaction (CASSI) method,[33] developed to compute transition properties from nonorthogonal state functions, is use here to compute the transition dipole moments. It is our experience that the transition dipole moment is not significantly affected by remaining correlation effects.[34] In the formula for the oscillator strength the energy differences corrected for the second-order perturbation method (PT2F) were used. This approach for the oscillator strength is by now well documented in a number of applications.[2,22,27-29]

2C. CASPT2 Method. The CASPT2 method[26] computes the first-order wave function and the second-order energy in the full CI space without any further approximation, with a CASSCF wave function constituting the reference function. The zeroth-order Hamiltonian is defined as a Fock type one-electron operator and is constructed such that a Möller–Plesset type perturbation theory is obtained in the closed-shell single-determinant case. Two different formulations of the zeroth-order Hamiltonian are possible: one which utilizes only the diagonal part of the Fock matrix (called PT2D) and one which includes also the nondiagonal elements (PT2F). It is only the PT2F approach that leaves the zeroth-order Hamiltonian invariant with respect to rotations among the molecular orbitals. Earlier studies[22] have shown that this invariance is important in describing Rydberg states. We shall, therefore, only present the PT2F results from the present study. The CASPT2 program calculates the weight, ω, of the CASSCF reference in the first-order wave function. This weight is a measure of how large a fraction of the wave function is treated variationally. Normally, one requires ω to be about the same for the ground and the excited states in order for the calculation to be balanced with respect to the treatment of electron correlation. In all the cases, the 1s electrons were not correlated.

All calculations have been performed on the IBM 9021/500-2VF computer at the University of Valencia using the MOLCAS-2 quantum chemistry software,[35] which includes the CASPT2 program as one module.

3. Experimental Methods

The experimental methods have been described previously in detail.[3b,36] Briefly, the optical spectrum of room temperature, gas-phase samples were measured with a Cary 15 spectrophotometer with a resolution of approximately 10 cm^{-1}. This is smaller than the observed bandwidths. The sample pressures in the 10-cm cell were between 0.1 and full vapor pressure, 22 Torr.

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(30) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070.

(31) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(32) Lorentzon, J.; Fülscher. M. P.; Malmqvist, P.-A.; Roos, B. O. To be published.

(33) (a) Malmqvist, P.-A. *Int. J. Quantum Chem.* **1986**, *30*, 479. (b) Malmqvist, P.-A.; Roos, B. O. *Chem. Phys. Lett.* **1989**, *155*, 189.

(34) Malmqvist, P.-A.; Roos, B. O.; Fülscher, M. P.; Rendell, A. *Chem. Phys.* **1992**, *162*, 359.

(35) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-A.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS, Version 2*; University of Lund, Sweden, 1991. The program can be obtained in versions for IBM VM/XA and AIX (for RS/6000 workstations) by contacting B. O. Roos.

(36) Xing, X.; McDiarmid, R.; Philis, J. G.; Goodman, L. *J. Chem. Phys.* **1993**, *99*, 7565.

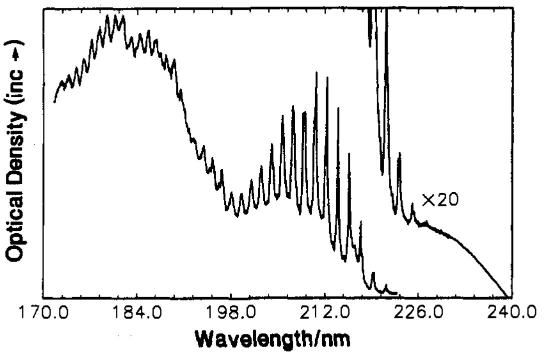

Figure 1. Optical absorption spectrum of gaseous, room temperature norbornadiene.

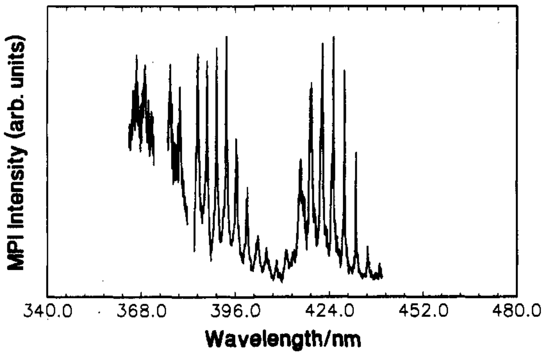

Figure 2. (2+1) resonant-enhanced multiphoton ionization spectrum of jet-cooled norbornadiene excited with linearly polarized light.

The REMPI spectrum was obtained on a conventional supersonic molecular beam coupled with a time of flight (TOF) mass spectrometer. The molecular beam was obtained by expansion of 3 atm of Ar seeded with norbornadiene through a pulsed 500-μm nozzle into a chamber pumped by two turbomolecular pumps. The laser system was a conventional injection-seeded Quanta-Ray YAG pumped dye system. Circular or linear polarization of the laser light was produced by a double- and single-Fresnel rhomb arrangement (full details of the experimental setup are presented in ref 36). The spectra were not normalized for the wavelength dependence of the light intensity. Although the ions of different masses were separated and individually detected, the spectrum obtained was mass-independent.

Norbornadiene was purchased from Wiley Organics and vacuum distilled when used. Chromatographic grade argon (99.995%) was used as supplied.

4. Experimental Results and Analysis

The optical absorption spectrum of norbornadiene from 240 to 170 nm (5.2–7.2 eV) is presented in Figure 1. This spectrum is better resolved than, but similar in appearance to, the previously published optical spectrum of norbornadiene.[8] It is composed of a large number of sharp bands superimposed on three broad, structureless bands. The structureless bands extend from 240 to 225 nm, 218 to 195 nm, and 195 to 175 nm. The sharp bands appear to run roughly continuously across the spectral region studied here, have an average spacing of approximately 360 cm^{-1}, and broaden toward the blue. The positions of all peaks in the spectrum were measured.[37]

The REMPI spectrum of the equivalent transition energy region of jet-cooled norbornadiene excited with linearly polarized light is presented in Figure 2. The small gaps between the different spectral regions are due to technical limitations on our ability to scan the entire region with our laser system. All measurements, except for a small region around 380 nm, were made with approximately the same power density in the exciting light; the relative intensities of the different regions presented in the figure are, therefore, roughly correct. As observed in the optical spectrum, the REMPI spectrum appears to be composed of an almost continuous array of structured bands, the spacing between bands is approximately 360 cm^{-1}, and the bands appear to broaden toward the blue. The positions of all bands were measured. Polarization-selected measurements were made throughout the REMPI spectrum. It has been previously demonstrated that for two-photon resonances this technique can be used to differentiate totally symmetric (i.e. A_1) transitions from non-totally symmetric transitions.[38] The REMPI system from 440 to 415 nm (experimental wavelength) is not totally symmetric. Since it is optically allowed, it must be B_1 or B_2. The REMPI system from 410 to 385 nm and the fragmentary system(s) between 365 and 383 nm are both A_1.

Although the general forms of the structured systems appear to be similar in the REMPI and optical absorption spectra, there are two immediately obvious differences between the two spectra: the lower energy bands are much sharper in the REMPI spectrum than in the optical spectrum and there are no diffuse bands underlying the narrower bands in the REMPI spectrum. The difference in bandwidth is trivially explained as due to rotational narrowing in the colder (approximately 10 K) jet-cooled sample compared with the room temperature optical sample. The other difference, the absence of diffuse bands underlying the narrow bands in the REMPI spectrum, bears on the assignments of these transitions and will be discussed below.

A detailed comparison of the narrow bands present in the optical and REMPI spectra demonstrates that no bands are present in the REMPI spectrum that are not also present in the optical spectrum once trivial exclusions are made for closely spaced subbands revealed in the better resolved REMPI spectrum. Thus, no A_2 transitions (i.e. transitions forbidden under one-photon selection rules but permitted under two-photon selection rules) are observed. By contrast, a few isolated bands are present in the optical spectrum that are absent from the REMPI spectrum. These include one of the closely spaced bands around 192.5 nm and the strong band at 189.5 nm. The weak, sharp bands that interdigitate with the stronger bands in the 180- and 190-nm region of the optical spectrum may also be absent from the REMPI spectrum, but it is difficult to determine because of the high noise level in this spectral region. There are also differences in the relative intensities of the sharp transitions as observed by the two experimental techniques; the lower members of each electronic transition are relatively stronger in the REMPI spectrum than in the absorption spectrum. This is most apparent around the beginning of the lowest energy structured system. This and the observed broadening of the subbands of each transition arise from a decrease in lifetime with increasing excess energy in each Rydberg state and will be presented more fully elsewhere.[37] In the current investigation this difference in experimental Franck–Condon structures was simply used, together with the shape of the ionization spectrum, polarization data, and comparisons between the vibrational substructures of the 440–415 and 410–385-nm spectral regions of the better resolved REMPI spectrum, to determine the origin, vibrational structure, and maximum of each of the structured transitions.

To determine the number of discrete electronic transitions giving rise to the narrow spectral bands and their properties, first the width of the photoelectron spectrum of the lowest enery ionization was considered. This band is 0.35 eV from its origin to its peak.[24] By comparison, the width of the lowest energy structured system observed here is around 0.32 eV (orig – peak). These two observations suggest that the orig – peak separation of each Rydberg transition will be around 0.32 eV. Next, the previously

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[37] Xing, X.; Gedanken, A.; Sheybani, A.-H.; McDiarmid, R. *J. Phys. Chem.*, in press.

[38] McClain, W. M.; Harris, R. A. In *Excited States*; Lim, E. D., Ed.; Academic: New York, 1977; Vol. 3 p 1.

Table 2: Experimental Spectrum of Norbornadiene

transition	experimental symmetry	origin (eV)	peak (eV)
$b_1 \rightarrow 3s$	$\neq {}^1A_1$	5.61	5.85
NV_1	allowed	≈5.74	≈6.0
$b_1 \rightarrow 3p$	${}^1A_1$	6.16	6.40
NV_2	allowed	≈6.3–6.4	≈6.7
$b_1 \rightarrow 3d$	allowed	<6.5	6.6
$a_1 \rightarrow 3s$	${}^1A_1$	6.54	6.91

noted subband intensity differences between the optical and REMPI spectra were used to identify the different origins. A detailed analysis of the 440–415- and 410–385-nm regions of the better resolved REMPI spectrum was also used to identify band origins.[37] From the above bandwidth analysis, the origins were initially assumed to lie approximately 0.35 eV to the red of the local maxima. Four overlapping transitions were thereby deconvoluted. Two transitions, those running from (the one-photon wavelengths) 220 to 208 and 205 to 192 nm, have comparable intensities. The weak system interleaving the stronger peaks between (the one-photon wavelengths) 190 and 180 nm is much weaker. The subbands of the highest energy system (188–175 nm) have become so broad that it is difficult to determine the intensity of the transition, but it is clearly very strong. Finally, the symmetries of the transitions were deduced to the greatest extent possible from the polarization-selected results. A summary of the experimental conclusions is presented in Table 2. The energies of the transitions reported in Table 2 are included in the fourth column of Table 3. Although many of these correspond with those previously reported, column 5, the experimental assignments are now based on the symmetry and optical properties of the observed transitions as well as the energies, hence are more certain.

In summary, the main experimental findings of this optical and REMPI spectroscopic investigation of norbornadiene are (1) a broad, almost structureless transition appears to underlie the long progression(s) of sharper bands in the optical spectrum. The former is absent from the REMPI spectrum. (2) No A_2 bands are observed between 7.3 and 5.2 eV. (3) Four discrete structured transitions appear in the spectral region investigated here. The maximum of each structured transition is approximately 0.3 eV above its origin. Similar origin - peak displacements appear to be present in the structureless transitions, but this is less certain. (4) The structured bands observed in the REMPI spectrum between 440 and 415 nm (5.6–6.0 eV) are not A_1. (5) The structured bands observed to the blue of 410 nm are A_1. (6) The transitions observed between 440 and 415 and between 410 and 385 nm (5.6–6.0 and 6.0–6.4 eV) have comparable intensities.

5. Theoretical Results and Analysis

The numerical results of the theoretical portion of this investigation are collected in Table 3. The first column identifies the different excited states of norbornadiene. The second and third columns give the vertical transition energies obtained by the CASSCF and PT2F calculations, respectively. The difference between the CASSCF and PT2F energies is a measure of the contribution of dynamic correlation to the energy of a state. Column 4 contains the experimental transition energies obtained in the current investigation. They are correlated with their corresponding calculated energies by symmetry and transition type. Other experimental results are given in column 5. In the remainder of this table, ω shows the weight of the CASSCF reference function in the first-order wave function (PT2F), μ is the dipole moment computed at the CASSCF level (in atomic units, and $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are the expectation values (in (atomic units)^2) of x^2, y^2, and z^2, respectively. The latter can be used to identify the nature of a state. Oscillator strengths obtained with the CASSI method are given in column 11. *Ab initio* energies and oscillator strengths obtained in previous calculations are given in columns 12–14.

Detailed information about the CASSCF wave functions for the ground and valence excited states is given in Table 4. Summarized there are the most important configurations and the number and the summed weights of singly (S), double (D), and triply (T) excited configurations with coefficients larger than 0.05 in each of the valence states of norbornadiene.

The singlet excited states were initially identified on the basis of their dominant orbital configurations. In addition, a comparison of the CASSCF and PT2F results demonstrates that dynamic correlation effects have larger contributions to the excitation energy of valence states than of Rydberg states. Accordingly, the value of ω (the weight of the CASSCF reference function in the first-order wave function) for a valence state is somewhat smaller than it is in the ground state, whereas the values of ω of Rydberg states are almost identical to that of the ground state. In general, Rydberg states are much less affected by electron correlation than valence states; norbornadiene presents however a few exceptions.

Another general observation is that the $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ values of the singlet Rydberg states are appreciably larger than those of the ground and singlet excited valence states. Those of the valence excited states are somewhat larger than that of the ground state, indicating a certain amount of valence–Rydberg mixing. An exception to this observation is the 6^1A_1 state, which is free of Rydberg character. The detailed interpretation of the results presented in Tables 3 and 4 is discussed below.

Valence Excited Singlet States (1^1A_2, 1^1B_2, 2^1B_2, 5^1A_2, and 6^1A_1). The lowest singlet excited state is of A_2 symmetry. That the lowest singlet → singlet transition is optically forbidden was clearly established by Doering and McDiarmid.[12] The vertical excitation energy calculated at the PT2F level, 5.28 eV, is in agreement with the observed value of 5.25 eV.[12] This transition was observed in an electron-impact study reported by Frueholz *et al.*[10] and has been also reported by Allan.[15] It appears as a shoulder centered at 5.4 eV in the optical[4,6,7] and CD[11] spectra.

The simple theoretical models also predict the lowest singlet excited state of norbornadiene to be A_2.[4,5] Since (Table 4) the CASSCF wave function of the 1^1A_2 state is dominated by the singly excited configuration ($b_1 \rightarrow b_2$), it is not surprising that the RPA energy,[13] 5.43 eV, is in reasonable agreement with the current calculation and with experiment. The CIS result,[14] by contrast, has a larger deviation. This is probably due to an inadequate treatment of electron correlation, especially the dynamic σ polarization effects, which in the present calculation decrease the excitation energy by 2.9 eV.

The next valence excited state is the 1^1B_2 state. In the present study this state appears at 6.20 eV. It is the ${}^1B_2^-$ state, arising from a mixture of the configurations ($a_1 \rightarrow b_2$) and ($b_1 \rightarrow a_2$). The computed intensity is relatively low, 0.0081. In this energy region the experimental spectrum shows narrowly spaced bands superimposed on much broader bands. Although a question has been raised as to the number of transitions these features represent,[12] comparisons of the low-pressure gas-phase absorption spectrum with those obtained at high pressures or in the solid phase,[8] the analysis of the electron energy loss spectrum,[10,12,15] and comparisons of the optical absorption and REMPI spectra unambiguously demonstrate the existence of transitions to two states of different character in this energy range. The transitions are assigned as a structured Rydberg transition and an underlying valence transition. The valence transition has its maximum around 6 eV. Considering the uncertainty in the experimental determination of the peak location and the expected error bars of the calculation, the agreement between theory and experiment is satisfactory.

Table 3: Calculated and Experimental Excitation Energies (in eV) and Other Properties of the Vertical Excited States of Norbornadiene

							total[c]			osc strength		other results	
state	CASSCF	PT2F	current exp	other exp	ω[a]	μ[b]	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle a^2 \rangle$	this work	previous[d]	RPA[d]	CIS[e]
ground state (1^1A_1)					0.75	+0.046	−31.9	−28.9	−32.9				
Singlet States													
$1^1A_2(V_1)$	8.18	5.28		5.23,[f,g] 5.25[h]	0.69	+0.770	−34.5	−45.8	−47.9		forbidden	5.43	6.00
$1^1B_1(b_1 \rightarrow 3s)$	6.26	5.73	5.85		0.73	+0.688	−55.0	−57.5	−57.5	0.0112	0.0181	6.18	
$2^1A_2(b_1 \rightarrow 3p_y)$	6.88	6.03			0.73	+1.063	−45.2	−90.0	−52.5		forbidden	6.77	
$1^1B_2(V_2)$	9.42	6.20	6.0	5.89,[i] 5.95,[f,h] 5.92[g]	0.68	+0.727	−43.7	−53.7	−42.7	0.0081	0.1536	6.75	6.67
$2^1A_1(b_1 \rightarrow 3p_x)$	6.24	6.33	6.40	6.38,[h] 6.35[g]	0.72	+0.943	−95.7	−48.9	−55.2	0.0105	0.0295	6.49	
$2^1B_1(b_1 \rightarrow 3p_z)$	6.72	6.33			0.73	−0.321	−46.1	−47.4	−98.8	9×10^{-6}	0.0073	6.81	
$3^1A_2(b_1 \rightarrow 3d_{yz})$	7.38	6.34			0.72	−1.925	−43.7	−84.1	−85.5		forbidden	7.40	
$2^1B_2(V_3)$	9.78	6.48	6.7	6.65[h,g]	0.66	−0.171	−46.8	−47.0	−38.5	0.3434	0.1314	8.57	7.49
$3^1B_2(b_1 \rightarrow 3d_{xy})$	7.42	6.50	6.6		0.73	−0.219	−81.2	−88.8	−50.0	0.0033	0.0473	7.10	
$3^1A_1(a_1 \rightarrow 3s)$	6.70	6.67	6.91	6.85,[h] 6.84[g]	0.69	+0.534	−55.8	−59.0	−57.5	0.0481	0.0209	7.37	
$3^1B_1(a_1 \rightarrow 3p_x)$	8.00	6.75			0.68	+0.421	−97.0	−48.0	−52.7	0.0011	0.0001	7.82	
$4^1B_2(a_1 \rightarrow 3p_y)$	8.05	6.77			0.72	+0.352	−55.8	−94.3	−52.0	0.0102	0.0074	7.73	
$4^1B_1(b_1 \rightarrow 3d_{x^2-y^2})$	7.11	6.79			0.74	−0.025	−75.9	−101.2	−56.9	0.0058	0.0166	7.20	
$5^1B_1(b_1 \rightarrow 3d_{z^2})$	7.21	6.92			0.74	−0.955	−78.9	−49.4	−112.5	0.0088	0.0030	7.36	
$4^1A_1(b_1 \rightarrow 3d_{xz})$	6.75	6.94		7.2[h,g]	0.73	−1.664	−92.4	−47.7	−97.0	0.0016	0.0002	7.21	
$5^1B_2(a_1 \rightarrow 3d_{yz})$	8.46	7.27			0.72	−0.777	−46.1	−89.0	−92.6	0.0216			
$5^1A_1(a_1 \rightarrow 3p_z)$	7.15	7.29			0.71	−0.221	−47.3	−48.1	−98.4	0.0032	0.0019	7.73	
$4^1A_2(a_1 \rightarrow 3d_{xy})$	8.55	7.29			0.72	+0.062	−87.0	−91.0	−50.9		forbidden		
$5^1A_2(V_4)$	10.40	7.36		7.50[h]	0.68	−0.215	−46.8	−52.0	−38.3		forbidden	9.05	7.32
$6^1B_1(a_1 \rightarrow 3d_{xz})$	8.48	7.39		7.65[h]	0.71	−0.473	−93.0	−46.5	−97.1	0.0213			
$6^1A_1(V_5)$	7.97	7.49			0.50	+0.355	−29.4	−28.5	−31.0	0.0002			6.98
$7^1A_1(a_1 \rightarrow 3d_{x^2-y^2})$	7.55	7.74		7.9[h]	0.69	−0.087	−72.3	−102.2	−61.3	0.0176			
$8^1A_1(a_1 \rightarrow 3d_{z^2})$	7.65	7.86		8.00[h]	0.70	−0.686	−87.6	−48.7	−108.9	0.0212			
Triplet States													
$1^3A_2(T_1)$	3.89	3.42		3.4,[f] 3.47[g]	0.73	+0.063	−31.1	−30.0	−33.4				
$1^3B_2(T_2)$	4.21	3.80		3.9[f,g]	0.72	+0.047	−31.8	−29.9	−32.8				

[a] The weight of the CASSCF reference function in the first-order wave function. [b] Dipole moment (CASSCF) in au. [c] Expectation value (CASSCF) of x^2, y^2, and z^2 (in au^2). [d] RPA results from ref 13. [e] CIS results from ref 14. [f] Electron-impact data, ref 10. [g] Electron-impact data, ref 15. [h] Electron-impact data, ref 12. [i] UV absorption data, ref 8.

Table 4: CASSCF Wave Functions for Norbornadiene: Principal Configurations, Weights, and Number (Weights) of Singly (S), Doubly (D), and Triply (T) Excited Configurations[a] with Coefficients Larger Than 0.05

			no. conf (weight)		
state	principal configurations	%	S	D	T
ground state (1^1A_1)	$(a_1)^2(b_1)^2$	91.1		5 (8.7%)	
1^1A_2	$(a_1)^2(b_1)^1(b_2)^1$	74.4	6 (98.8%)		
$1^1B_2^-$	$(a_1)^1(b_1)^2(b_2)^1$	44.0	6 (98.2%)		1 (0.4%)
	$(a_1)^2(b_1)^1(a_2)^1$	37.1			
$2^1B_2^+$	$(a_1)^1(b_1)^2(b_2)^1$	40.1	6 (95.6%)		4 (3.8%)
	$(a_1)^2(b_1)^1(a_2)^1$	49.5			
5^1A_2	$(a_1)^1(b_1)^2(a_2)^1$	73.9	6 (97.6%)		2 (1.1%)
6^1A_1	$(a_1)^2(b_2)^2$	35.4		5 (99.8%)	
	$(a_1)^1(b_1)^1(b_2)^1(a_2)^1$	21.7			
	$(b_1)^2(b_2)^2$	20.9			
1^3A_2	$(a_1)^2(b_1)^1(b_2)^1$	72.5	2 (95.7%)		2 (4.3%)
	$(a_1)^1(b_1)^2(a_2)^1$	23.2			
1^3B_2	$(a_1)^1(b_1)^2(b_2)^1$	48.1	2 (95.1%)		2 (4.9%)
	$(a_1)^2(b_1)^1(a_2)^1$	47.0			

[a] With respect to the ground-state principal configuration.

Two other calculations of the $B_2^- \leftarrow X$ transition have been carried out. The RPA calculation[13] places this transition at 6.75 eV with an intensity of 0.15. The RPA results thus disagree with the experimental as to both transition energy and intensity. In addition to being inconsistent with the experimental results, such a relatively large intensity is discordant with the minus character of the state. The B_2 states are quite sensitive to the combination of the singly excited configurations ($a_1 \rightarrow b_2$) and ($b_1 \rightarrow a_2$) in the multiconfigurational wave function; hence, a balanced treatment of the singly excited configurations is required for the proper description of the B_2 states. In the RPA results reported by Galasso,[13] the weights of these configurations are 67 and 23% compared to 44 and 37% of the CASSCF wave function (cf. Table 4). The CIS calculation, on the other hand, yields a computed value for a 1^1B_2 state more than 1.1 eV higher than that calculated here, which is itself about 0.2 eV higher than the observed value. This is even greater than the discrepancy between the CIS and PT2F calculations of the excitation energy to the A_2 state. Thus, neither of the limited *ab initio* methods seem capable of giving an adequate characterization of the B_2^- valence state of norbornadiene.

The third valence excited state is the most intense feature in the system. The calculation places the 2^1B_2 state at 6.48 eV with an intensity of 0.34. This is the $^1B_2^+$ state. It corresponds to the 6.65-eV peak of the energy loss spectra reported by Doering and McDiarmid[12] and the continuous absorption underlying the structured systems between 195 and 180 nm (6.5–6.9 eV) displayed in Figure 1. Previously, the $^1B_2^+$ valence state and the Rydberg ($a_1 \rightarrow 3_s$) transition were proposed as possible assignments of the feature found at 6.85 eV[10] or at 6.88 eV.[8] As demonstrated here, by comparing the optical and REMPI spectra as was done in the spectral region of the B_2^- state, above, there are two different types of transitions between 6.5 and 6.9 eV. One of these is a valence transition centered around 6.7 eV. The other is a Rydberg transition, which will be discussed below. The RPA study[13] places the second $^1B_2$ valence excited state at 8.57 eV with an intensity of 0.13. The CIS calculation[12] places this second $^1B_2$ state at 7.49 eV but does not designate whether these energies correspond to the $^1B_2^+$ valence state or to a $^1B_2$ Rydberg state.

The 5^1A_2 and 6^1A_1 valence states are calculated to be close in energy with computed values of 7.36 and 7.49 eV, respectively. The transition from the ground state to 5^1A_2 is optically forbidden; the transition from the ground state to 6^1A_1 is calculated to be very weak. The 6^1A_1 state differs from the other valence excited states in corresponding essentially exactly in size with the ground state. As detailed in Table 4, this state is dominated by doubly excited configurations, and no Rydberg mixing occurs. By contrast, the other valence singlet states are mainly described by singly excited configurations. Valence mixing with the corresponding nearby Rydberg states of the same symmetry seems to occur more easily here. As discussed elsewhere,[22] the valence–Rydberg mixing may not be properly taken into account at the CASSCF level. Nevertheless, compared to the corresponding Rydberg state, the diffuse character of the valence states is not large. The present study supports the assignment of the second valence state of $^1A_2$ symmetry around 7.5 eV, deduced from the electron-impact investigation.[12] It also supports the previous conclusion that the second $^1B_2$ transition lies lower in energy than the second $^1A_2$ transition.[12] The computed intensity for the 6^1A_1 state is very low, consistent with its doubly excited nature and with the experimental inability to observe this transition. The RPA[13] calculation places the second $^1A_2$ valence excited state at 9.05, much too high in energy, and does not report the doubly excited valence state. The CIS calculation[14] places an $^1A_2$ state at 7.32 eV and an $^1A_1$ state at 6.98 eV. However, as the characters of the states are not identified, and since Rydberg states of these symmetries also occur at these energies, it is not possible to correlate these states with those calculated here or in the RPA calculation.[13]

Rydberg States. The first and second vertical ionization potentials of norbornadiene lie within 1 eV of each other.[18] As a result, corresponding members of Rydberg series converging to these two ionization potentials are expected to lie within 1 eV of each other. As 1 eV approximates the usual 3s and 3d Rydberg-state separation, Rydberg states leading to the two ionization limits are expected to overlap in energy even for early series members. Here we discuss PT2F energies and assignments for the states described by excitations out of the HOMO, $6b_1$, and HOMO-1, $10a_1$, to the 3s and to the different components of the 3p and 3d Rydberg orbitals and compare them with the experimental assignments and the results of previous calculations.

$b_1 \rightarrow$ 3s (1^1B_1). The calculated vertical transition energy from the ground to the first 3s Rydberg state is 5.73 eV. The oscillator strength is around 0.01. As discussed above, this energy corresponds to the experimental energy at which a sharply structured transition overlaps an exceedingly diffuse transition in the optical spectrum and only the sharp structured transition is observed in the REMPI spectrum. The structured transition is identified as a Rydberg transition from the ground to a B_1 or B_2 state. The peak intensity of this transition corresponds to a transition energy of 5.83–5.88 eV. The calculated transition energy is, therefore, in agreement with experiment, and the observed symmetry is consistent with this assignment. Both the RPA[13] and the CIS[14] calculation overestimate the transition energy.

$b_1 \rightarrow$ 3p (2^1A_2, 2^1A_1, and 2^1B_1). The 2^1A_2 state is calculated here to lie 6.03 eV above the ground state. Both the 2^1A_1 and 2^1B_1 states are calculated to lie 6.33 eV above the ground state, the former with a similar intensity to the 3s Rydberg state, the latter exceedingly weak. As discussed in the experimental part of this study, no experimental evidence is found for an $^1A_2$ transition in this energy range. One transition is observed here by both optical and REMPI spectroscopies. By polarization-selected REMPI spectroscopy it is identified as an $^1A_1$ transition. Its peak is around 6.4 eV. It is about equal in intensity to the 5.9-eV transition. There is, therefore, agreement between the symmetry of the observed transition and that calculated to be the more intense optically allowed transition, agreement between the relative observed and calculated intensities of the $b_1 \rightarrow$ 3s and 3p(A_1) Rydberg transitions, and agreement between the calculated and observed transition energies for the $A_1 \leftarrow X$ transition. The RPA calculation[13] places the $b_1 \rightarrow$ 3p(A_1) transition lowest of the three $b_1 \rightarrow$ 3p transitions, at 6.49 eV, in contrast to our finding that this state is one of the higher of such transitions. Thus, the apparent agreement between the results of the RPA calculation[13] and the experiment may be fortuitous. The CIS calculation[14] placed all states of the same symmetries as the 3p Rydberg states higher in energy than either the current or the RPA calculation.

$b_1 \rightarrow$ 3d (3^1A_2, 3^1B_2, 4^1B_1, 5^1B_1, and 4^1A_1). These five members of the 3d series have been computed to lie in the energy range 6.34–6.94 eV. The lowest allowed such transition is calculated to be the 3^1B_2 state at 6.50 eV and to have an intensity approximately one-third that of the 3s and 3p(A_1) transitions discussed above. It is likely that this corresponds to the weak system observed between the stronger bands around 189 nm (6.6 eV) in the optical spectrum. The RPA study[13] found these states in the energy range 7.10–7.40 eV.

$a_1 \rightarrow$ 3s (3^1A_1). The energy of the first component of the Rydberg series to the second ionization potential is computed to be 6.67 eV. It is calculated to be the second strongest transition in the molecule. This agrees well with the strong band system observed here between 189 and 178 nm in the optical spectrum and observed to be $^1A_1$ in the REMPI spectrum. The peak of this system is estimated to be 6.9 eV. The existence of this transition was previously deduced from the electron energy loss investigations.[10,12,15] The RPA calculation[13] places the state at 7.37 eV.

$a_1 \rightarrow$ 3p and 3d. Although the energies and intensities of these transitions have been calculated, neither high resolution nor polarization-selected REMPI spectra exist for these transitions, so experimental symmetries of the transition moments are not known. Since many closely spaced states are calculated here, coincidence between an experimental and a calculated transition energy may be accidental. In this spectral region, therefore, the experimental and theoretical results can best be combined to deduce spectral assignments, but neither can be said to confirm the other. Five further peaks are observed in the energy loss spectrum. These are centered at 7.2, 7.45, 7.65, 7.9, and 8 eV. They have been previously assigned on the basis of their electron-scattering and quantum defects. Nine transitions have been calculated to lie in this energy range, and the four $b_1 \rightarrow$ 4s and 4p transitions, which have not been calculated, should also lie here. If we assume that transitions to the $n = 4$ are weaker than those to $n = 3$,[39] and that only the stronger of the calculated transitions are observed, we arrive at the correlation entered in the lower half of column 5 of Table 3. These correlations yield a mean discrepancy between experiment and theory of around 0.25 eV, somewhat larger than that obtained above for the experimentally assigned transitions. It is unclear whether this increased discrepancy is due to mistakes in the experimental–theoretical correlations or to uncertainties in the calculations. Errors of this size have occasionally been obtained in earlier applications using the same approach and basis set.

Additional Singlet States. The calculation presented so far includes 23 singlet excited states, five valence states, and the $b_1 \rightarrow$ 3s, 3p, 3d and the $a_1 \rightarrow$ 3s, 3p, 3d Rydberg states. The CASSCF calculations were performed as an average over all states of a given symmetry needed to describe these designated states plus additional (one to two) roots of each symmetry. This was done to analyze the importance of $\pi \rightarrow \sigma^*$ transitions. A total of eight additional states were considered. Seven of them, of the $\pi \rightarrow \sigma^*$ type with Rydberg mixing, lie in the energy range 8.20–9.14 eV and have relatively low intensities. The transition to the values $^1B_1(a_1b_1 \rightarrow b_2b_2)$ state, which has no Rydberg mixing and is also very weak, is placed at 8.96 eV. From this we conclude that the states described mainly by $\pi \rightarrow \sigma^*$ excitations do not play an important role in the lower energy electronic spectrum of norbornadiene. To understand the more energetic part of the spectrum, the $b_1 = n = 4$ Rydberg transitions and maybe also the $\sigma \rightarrow \pi^*$ transitions should be considered before $\pi \rightarrow \sigma^*$ excitations. Since the former two types of excitations were not considered in the present work, the basis set employed here has not enough

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(39) Herzberg, G. *Spectra of Diatomic Molecules*; Nostrand: New York, 1950, p 383.

flexibility to describe the $n = 4$ Rydberg series and the active spaces chosen cannot describe $\sigma \rightarrow \pi^*$ states.

Triplet States. The two lowest energy triplet states of norbornadiene were also treated in this calculation. These states occur at 3.42 eV (1^3A_2) and 3.80 eV (1^3B_2). The lowest energy transition observed in the norbornadiene spectra has an apparent Frank–Condon envelope extending from about 2.9 to 4.5 eV.[8,13] Frueholz *et al.*[10] suggested this band as due to two overlapping singlet → triplet transitions and estimated the intensity maxima of these transitions to be approximately 3.5 and 3.9 eV. More recently Allan reported[15] the vibrationally resolved electron energy loss spectrum of norbornadiene in this energy region. He confirmed the band maxima of the transitions. Our calculated results are in agreement with the experimental results.

6. Discussion

In this section we will first assess the ability of the theoretical method employed here to handle indirect conjugation and σ,π interaction through a comparison of the accuracy of these results with those previously obtained for cyclopentadiene, a similar-sized molecule lacking indirect conjugation and σ,π interactions. We will then discuss correlations among the energy levels of the related series of molecules, *cis*-butadiene, cyclopentadiene, and norbornadiene. Finally, we will consider some further features of this calculation and compare it with some other calculations carried out on these molecules. These topics will be treated in turn.

The CASPT2 method has in a number of studies been shown to be accurate to better than 0.2 eV for almost all calculated excitation energies. For instance, we have recently reported[2a] results for the valence and Rydberg states of cyclopentadiene, in which an average deviation of 0.04 eV was found for the vertical transition energies of those transitions which could be correlated by symmetry, intensity, and character with experimental transitions. As can be seen in Table 3, a somewhat larger deviation from the experimental data is obtained for the computed vertical transition energies in norbornadiene. One of the reasons for the relatively larger deviation of the computed energies in this case can be ascribed to the valence–Rydberg mixing. As explained in detail elsewhere,[22a] an artificial mixing of Rydberg and valence character in the reference function is not fully compensated in a low-order perturbation calculation. The errors in the computed excitation energies are unusually large when this occurs. Similar deviations (+0.3 to –0.2) were found[22a] for that reason for the ^1B_u states of *trans*-butadiene. In norbornadiene the $^1B_2^-$ state has an error of 0.2 eV. The increased value $\langle r^2 \rangle$ compared to that of the ground state hints to a possible mixing with the Rydberg states of the same symmetry. An unusually large correlation contribution to the transition energy for the $b_1 \rightarrow 3d_{xy}$ Rydberg state, 3^1B_2, points in the same direction. Several of the Rydberg states are too low in energy. This again is an indication of erroneous mixing with valence excited states where the correlation contributions are larger.

An additional reason for deviations between computed and measured transition energies is also possible in norbornadiene that affects both computed and measured transition energies. The equilibrium geometries for all excited states studied here differ substantially from that of the ground state.[14,15,37] The resulting broad Franck–Condon envelopes introduce relatively large uncertainties into experimental band maximum determinations. In addition, because of the steep curvatures of the excited-state potential energy surfaces at the ground-state equilibrium geometry, small errors in the geometry used for the ground state may lead to significant errors in computed vertical transition energies. The experimental geometry determined by gas-electron diffraction was employed here, for which the estimated limits of errors in some of the geometrical parameters are somewhat large.[1] Not withstanding the slightly greater discrepancy between theory and experiment obtained here for norbornadiene than that obtained previously for cyclopentadiene, the calculation clearly accurately reproduces the excited-state manifolds of both molecules as to state energies, symmetries, and transition types.

The theoretical transition energies obtained for *cis*-butadiene (cB),[22b] cyclopentadiene (CP),[2a] and norbornadiene (NB) are presented in Table 5. The SCF orbital energies of the highest occupied and lowest empty π orbitals calculated for all molecules with comparable basis sets are also given here. The latter can be used in a simple way to rationalize the observed trends, by assuming that the relative transition energies are related to orbital energy differences between molecules. We start by noting that because the HOMO and HOMO-1 of cB and CP are more than twice as far apart as in NB, comparably promoted states will be further apart in the former two molecules than in the latter in the absence of interactions with states external to this one-electron scheme. At this level, the SCF orbital energies also prefigure the multiconfigurational wave functions; namely, the mixing of given excitations in the CASSCF wave function will depend on the relative energies of the corresponding configurations. It is clear from this compilation that in the absence of interactions with states external to this scheme, such as doubly promoted states, the spectra of NB and CP will be similar in character but the latter more widely spaced. In any case, the spectra can be interpreted in terms of the same basic trype of excitations.

The lowest singlet state is mainly represented by the HOMO→LUMO excitation, which is dipole-allowed in CP (and cB) and forbidden in NB and for which the excitation energies are of comparable magnitude. The second valence transition corresponds to a (HOMO-1→LUMO)–(HOMO→LUMO+1) excitation and is therefore weak. The most intense transition is to the analogous plus state. It is found at higher energy in CP than in NB—8.0 vs 6.5 eV experimentally, 7.9 vs 6.5 eV theoretically—consistent with the larger energy difference between the π_3 and π_1 (D_2) and π_4 and π_2 (D_3) orbital energies in CP than in NB. In the simple model presented above we expect the minus states of cB and CP to be about the above difference higher in energy than it is in NB. This is not born out in the calculations, 6.3 vs 6.0 eV. (The experimental vertical transition energy of this state is not known for CP.) As we hypothesized above, further analysis shows that in cB and CP this model is insufficient; in CP and cB the V_2, V_3, and V_5 transitions are all of A_1 symmetry and can interact. The contribution of doubly excited configurations in the $^1A_1^-$ state of CP and cB is significant, about 40 and 50%,[2b] respectively. This interaction causes a reduction in the energy of the lowest A_1^- state from that predicted by the simple orbital model discussed above. It is more pronounced in cB than in CP, according to the smaller D1 value in cB than in CP. The large weight of double excitations in the $^1A_1^-$ state also reduces the intensity of this state further relative to a "pure" minus state. Concomitant with this reduction in energy of the second $^1A_1$ state in CP and cB, the third $^1A_1$ state (that is, the $^1A^+$ state) is pushed up to above 8.5 eV. The doubly excited $^1A_1$ state of NB does not interact with any other valence excited states. It is calculated to appear at a moderate energy with a very weak intensity, in accordance with its "pure" doubly excited character. On the basis of the larger energy difference between the π_4 and π_1 orbital energies (D_4) in cB and CP than in NB, the V_4 transition is estimated to be very much higher in the former than in the latter.

Norbornadiene and cyclopentadiene have almost the same first vertical ionization potential.[18,19] They should, consequently, have similar manifolds leading to the lowest ionization potential. As noted in Table 5, the R_1 excitation energy and the average 3p (R_2) and 3d (R_3) transition energies are similar for NB and CP. Because *cis*-butadiene has a higher vertical ionization potential than NB or CP (see π_2 orbital energies), the R_1, R_2, and R_3 transitions lie at higher energies in this molecule. In addition,

Table 5: Calculated PT2F Excitation Energies (ΔE in eV)[a] and Oscillator Strengths for the Singlet States, in the Energy Range Below 8.5 eV, and the Two Lowest Triplet States in Norbornadiene (NB), Cyclopentadiene (CP), and *cis*-1,3-Butadiene (cB)

	NB			CP[c]			cB[d]		
state[b]	state	ΔE	osc	state	ΔE	osc	state	ΔE	osc
				Singlet States					
V_1: ($\pi_2 \rightarrow \pi_3$)	$^1A_2$	5.28		$^1B_2$	5.27	0.148	$^1B_2$	5.58	0.218
V_2: ($\pi_1 \rightarrow \pi_3$) ($\pi_2 \rightarrow \pi_4$)	$^1B_2^-$	6.20	0.008	$^1A_1^-$	6.31	0.0003	$^1A_1^-$	6.04	0.008
V_3: ($\pi_1 \rightarrow \pi_3$) ($\pi_2 \rightarrow \pi_4$)	$^1B_2^+$	6.48	0.343	$^1A_1^+$	7.89	0.442			
V_4: ($\pi_1 \rightarrow \pi_4$)	$^1A_2$	7.36		$^1B_2$					
V_5: (diex.)[e]	$^1A_1$	7.49	0.0002	$^1A_1$					
R_1: ($\pi_2 \rightarrow$ 3s)	$^1B_1$	5.73	0.011	$^1A_2$	5.65		$^1A_2$	6.05	
R_2: ($\pi_2 \rightarrow$ 3p)		6.23			6.26			6.67	
R_3: ($\pi_2 \rightarrow$ 3d)		6.70			6.88			7.39	
R_4: ($\pi_1 \rightarrow$ 3s)	$^1A_1$	6.67	0.048	$^1B_1$	7.95	0.025	$^1B_1$	8.44	0.046
R_5: ($\pi_1 \rightarrow$ 3p)		6.94							
R_6: ($\pi_1 \rightarrow$ 3d)		7.51							
				Triplet States					
T_1: ($\pi_2 \rightarrow \pi_3$) ($\pi_1 \rightarrow \pi_4$)	$^3A_2$	3.42		$^3B_2$	3.15		$^3B_2$	2.81	
T_2: ($\pi_1 \rightarrow \pi_3$) ($\pi_2 \rightarrow \pi_4$)	$^3B_2$	3.80		$^3A_1$	4.90		$^3A_1$	4.74	
				SCF Orbital Energies (eV)[f]					
$\epsilon(\pi_4)$		3.52			5.65			5.34	
$\epsilon(\pi_3)$		2.44			3.10			2.12	
$\epsilon(\pi_2)$		−8.60			−8.38			−8.69	
$\epsilon(\pi_1)$		−9.64			−11.27			−11.93	
$D_1 = \epsilon(\pi_3) - \epsilon(\pi_2)$		11.0			11.5			10.8	
$D_2 = \epsilon(\pi_3) - \epsilon(\pi_1)$		12.1			14.4			14.1	
$D_3 = \epsilon(\pi_4) - \epsilon(\pi_2)$		12.1			14.0			14.0	
$D_4 = \epsilon(\pi_4) - \epsilon(\pi_1)$		13.2			16.9			17.3	

[a] Average values for the 3p and 3d Rydberg states. [b] Referred to the NB system. In CP and cB the V_2, V_3, and V_5 transitions belong to the same symmetry and interact (see Discussion in the text). π_1, π_2, π_3, and π_4 correspond to the a_1, b_1, b_2, and a_2 π-derived orbitals of NB, and b_1, a_2, b_1, and a_2 π MOs of CP and cB, respectively. [c] Reference 2a. [d] Reference 22b. [e] State characterized by several doubly excited configurations (see Table 4). [f] SCF orbital energies for cyclopentadiene and *cis*-1,3-butadiene taken from ref 2b.

the calculated distance in energy between 3s Rydberg states obtained by exciting out of the (HOMO-1) and (HOMO), 1.3 eV, is about the same as the distance between the first and second vertical ionization potential in both NB and CP, 1.1 eV.[18,19]

Similar arguments can be employed to explain the trends for the lowest triplet states. The lowest triplet state is mainly described by the HOMO→LUMO excitation. The D_1 values are about the same in all three molecules. This is reflected in similar values for the T_1 energies. The simple orbital energy model does not allow for a more detailed discussion of the small relative energy differences. The smaller differences between T_1 and T_2 is correlated with the smaller difference between D_1 and D_2 in NB than in CP and cB, since the triplet states have no perturbation by doubly excited states. The similarity of the D_1, D_2, and D_3 orbital energy differences reflects the weaker coupling of the double bonds in NB.

A comparison of the CASSCF and PT2F calculations also reveals information about the different levels of calculation needed to describe different molecules and different excited states in these molecules. The CASSCF and PT2F energies obtained here for norbornadiene show that the contribution of dynamic correlation to state energies is greater for singly promoted valence than for Rydberg states. For the Rydberg states, the contribution of dynamic correlation to state energies is greater for promotions out of the second highest occupied molecular orbital than from the first. And, finally, the contribution of dynamic correlation to the state energy of the doubly promoted valence state is quite small, approximately the same as that observed for Rydberg states to the first ionization limit. The same has been observed in cyclopentadiene except that there the contribution of dynamic correlation to Rydberg-state energies is even smaller than that observed in norbornadiene. Since the two molecules are approximately the same size, we interpret this result to indicate that limited calculations are even less valid for nonplanar, strained molecules, like norbornadiene, than they are for simpler systems.

Semiempirical calculations have also been carried out on NB and CP, the former using the CNDOS/S+CISD approach,[14] the latter the QCFF+CISD method.[23] For norbornadiene, using the experimental geometry,[1] the first three singly electron promoted valence states were found at similar energies to those calculated here, $^1A_2$ at 5.25 eV, $^1B_2^-$ at 6.18 eV, and $^1B_2^+$ at 6.73 eV with the strongest intensity. The second A_2 state was obtained at 6.61 eV, which is much lower than the present result and even lower than the second B_2 state. In addition, the doubly excited A_1 state, which is found here to be above all the singly excited valence states, is calculated in the CNDO investigation to be the third excited valence state at 6.5 eV. This result is consistent with that obtained by the QCFF+CISD calculation on cyclopentadiene, in which the energy of the lowest one-electron-promoted excited state was calculated to be essentially the same as that calculated by the PT2F method and the doubly excited state significantly lower. These results and ours suggest that semiempirical schemes or empirical correlation correction methods that are parametrized with reference to singly excited valence energies may excessively correlate doubly excited states.

Finally, it might be worth noting that to reach a reasonable qualitative understanding of dienes, high-level calculations were required. First, near degeneracies were properly treated within the multiconfigurational CASSCF method. As applied to norbornadiene, the RPA technique does not appear to correctly treat these near degeneracies. The CASSCF wave function was subsequently used as a reference function in a multiconfigurational perturbational treatment. The latter accounts for dynamic correlation effects, which, since they contribute significantly to excited-state energies, are necessary for a quantitative theoretical study of the spectra. From this quantitative determination, a meaningful qualitative rationalization and relationship of the spectra in dienes could be achieved.

7. Conclusion

The results of a combined theoretical and experimental investigation of the lower energy region of the spectrum of norbornadiene have been presented above. The experimental investigation was performed to obtain the symmetries, characteristics, and vertical energies of the lower energy transitions of norbornadiene needed for a critical assessment of the calculated spectrum. The calculation was carried out to test the ability of the method to treat problems specific to norbornadiene—indirect conjugation and π,σ interaction in a strained molecule—but also common in complicated molecules. It was found that the calculation was able to successfully handle the problems. In this investigation we also compared the energy levels of the related series of dienes, *cis*-butadiene, cyclopentadiene, and norbornadiene, and assessed the accuracy of some *ab initio* and semiempirical calculations on these molecules. Our results indicate that current empirical schemes for handling correlation may be inadequate.

Acknowledgment. The research reported in this communication has been supported in part by a grant from the Swedish Natural Science Research Council (NFR), by IBM Sweden under a joint study contract, and by the Cooperación Científica-Técnica (Ministerio de Asuntos Exteriores) of Spain.