

## THE LOW-LYING EXCITED STATES OF WATER, METHANOL, AND DIMETHYL ETHER\*

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Received 23 April 1976

Improved virtual orbital (IVO) calculations have been performed on the low-lying excited states of water, methanol, and dimethyl ether using minimal basis sets of contracted gaussian functions augmented with diffuse s and p functions. In all three molecules the low-lying states correspond to excitations out of an oxygen lone pair orbital to an excited orbital having the basic character of a 3s or 3p Rydberg orbital centered on the oxygen. The 3s and 3p<sub>2</sub> Rydberg orbitals in water have especially large stabilities (term values) arising from favorable interactions with the electron-deficient hydrogens. Methylation diminishes this added stability in methanol and destroys it in dimethyl ether. The IVO calculations are used to assign the low-lying transitions in the optical and electron impact spectra of methanol and dimethyl ether.

### 1. Introduction

Water and its methyl derivatives, methanol and dimethyl ether, are prototypes for two important classes of organic molecules, namely, alcohols and ethers. Therefore, it is surprising that the excited states of water have only recently been well characterized and assigned [1-4], while the excited state assignments in methanol and dimethyl ether are in dispute [5,6]. The key point of contention in the latter case is the nature of certain low-lying states, i.e., whether they are valence or Rydberg in character. The higher lying observed transitions have been assigned to Rydberg series although the specific state assignments for methanol and dimethyl ether are not known. A detailed account of the electronic spectra of alcohols and ethers may be found in the recent critical review of Robin [7].

Since the states of water are well characterized [1,4], it is appropriate to relate them to those of methanol and dimethyl ether, taking into account the effect of methylation. Previously work [1,4,8] has demonstrated

that a semiquantitative determination of the excited state spectrum for water may be made with a simple, inexpensive technique known as the Improved Virtual Orbital (IVO) method [8]. In light of this success, IVO calculations on the low-lying excited states of methanol and dimethyl ether were performed and the results are reported herein.

### 2. Computational details

Ground state Hartree-Fock calculations were performed at the experimental geometries for water [9-13], methanol [14], and dimethyl ether [15]. The basis set employed in the calculations consisted of the Dunning [16] [2s, 1p/1s] contraction of the Huzinaga [17] [7s, 3p/3s] set of primitive gaussian functions augmented with two sets of diffuse s and p functions on the oxygen and carbon(s). The diffuse functions were chosen to provide a good description of 3s and 3p Rydberg orbital [18,39].

The low-lying excited states are obtained by exciting an electron from one of the two highest doubly-occupied orbitals,  $\phi_n$ , to an empty (or virtual) orbital,  $\phi_v$ . The one-electron excitations are combined with the appropriate spin function to obtain singlet and triplet

\* This work was supported in part by a grant (No. CHE73-05132) from the National Science Foundation.

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states. For all three molecules the two highest occupied orbitals correspond to the oxygen lone pairs. The symmetry designations for the lone pair orbitals are as follows:  $\text{H}_2\text{O}$  ( $C_{2v}$ ):  $n\pi = 1b_1$  and  $n\sigma = 3a_1$ ;  $\text{CH}_3\text{OH}$  ( $C_s$ ):  $n\pi = 2a''$  and  $n\sigma = 7a'$ ; and  $\text{CH}_3\text{OCH}_3$  ( $C_{2v}$ ):  $n\pi = 2b_1$  and  $n\sigma = 6a_1$ . The ionization potentials (IP) of the  $n\pi$  orbitals are lower by  $\sim 2$  eV than the IPs of the  $n\sigma$  orbitals so that the lower transitions arise from  $n\pi$ .

The excited state wavefunctions are obtained by solving for the virtual orbitals,  $\phi_v$ , with the correct variational equation for the orbital excitation  $\phi_n \rightarrow \phi_v$ :

$$H_v \phi_v = \epsilon_v \phi_v, \quad (1)$$

$$H_v = \sum_i^{\text{core}} (2J_i - K_i) + (J_n \pm K_n), \quad (2)$$

but *not* allowing the occupied orbitals to readjust. Since the  $H_v$  in (2) is independent of  $\phi_v$ , the entire spectrum of excited states is obtained by solving (1) once each for the singlet and triplet states. This leads directly to term values,  $|\epsilon_v|$ , for each of the excited states. The excitation energies are obtained from these term values as the difference of the orbital energies, or

using Koopmans' theorem [19], as the difference of the ionization potentials

$$\Delta E_{n \rightarrow v} = \epsilon_v - \epsilon_n = \text{IP}_n - \text{IP}_v. \quad (3)$$

Previous IVO calculations on  $\text{H}_2\text{O}$  [1,4,8],  $\text{C}_2\text{H}_4$  [20],  $\text{CO}$  [20],  $\text{N}_2$  [20], and  $\text{O}_2$  [21] have led to good values (0.1 to 0.2 eV errors) for the ionization potentials of Rydberg excited states, i.e., for  $\text{IP}_v$  or  $\epsilon_v$  [22]. The reason is that the correlation error in a Rydberg excited state is comparable to that in the positive ion because of the diffuse nature of the excited orbital. On the other hand, Hartree-Fock calculations generally lead to poor values for ground state ionization potentials,  $\text{IP}_n$  or  $\epsilon_n$ . Therefore, we employ the experimental value for  $\epsilon_n$  in (3) to calculate the excitation energy.

### 3. Results and discussion

#### 3.1. $\text{H}_2\text{O}$

The lowest vertical excitation energies are known to correspond to one-electron promotions from an oxygen lone pair into an  $n = 3$  Rydberg orbital on the

Table 1  
Basis set dependence of IVO calculations on the excited states of water (eV)

| Excitation               | State   | Present work | Winter et al. [1] | Hunt and Goddard [8] | Goddard and Hunt [4] | Best value [1] |
|--------------------------|---------|--------------|-------------------|----------------------|----------------------|----------------|
| $1b_1 \rightarrow 3sa_1$ | $^3B_1$ | 6.62         | 6.62              | 6.63                 | 6.68                 | 7.14           |
|                          | $^1B_1$ | 7.37         | 7.27              | 7.28                 | 7.30                 | 7.49           |
| $\rightarrow 3pb_2$      | $^3A_2$ | 9.29         | 8.79              | 8.83                 | 8.68                 | 9.1            |
|                          | $^1A_2$ | 9.56         | 9.13              | 9.20                 | 9.04                 | 9.2            |
| $\rightarrow 3pa_1$      | $^3B_1$ | 10.14        | 10.03             | 9.99                 | 9.96                 | 9.93           |
|                          | $^1B_1$ | 10.19        | 10.14             | 10.08                | 10.04                | 10.00          |
| $\rightarrow 3pb_1$      | $^3A_1$ | 9.93         | 9.71              | 9.85                 | 9.70                 | 9.81           |
|                          | $^1A_1$ | 10.18        | 10.38             | 10.26                | 10.16                | 10.17          |
| $3a_1 \rightarrow 3sa_1$ | $^3A_1$ | 9.16         | 8.97              | 9.01                 | 9.02                 | 9.35           |
|                          | $^1A_1$ | 9.98         | 9.85              | 9.94                 | 9.92                 | 9.73           |
| $\rightarrow 3pb_2$      | $^3B_2$ | 11.47        | 10.88             |                      | 10.81                | 11.1           |
|                          | $^1B_2$ | 11.81        | 11.52             |                      | 11.46                | 11.5           |
| $\rightarrow 3pa_1$      | $^3A_1$ | 12.03        | 11.86             |                      |                      | 11.8           |
|                          | $^1A_1$ | 12.32        | 12.49             |                      |                      | 12.1           |
| $\rightarrow 3pb_1$      | $^3B_1$ | 12.16        | 12.01             |                      |                      | 11.86          |
|                          | $^1B_1$ | 12.20        | 12.10             |                      |                      | 11.91          |

Table 2  
Low-lying excited states of water

| Excitation                         | State                       | Vertical excitation energy (eV)         |       | Oscillator strength<br>(molar extinction coefficient) |                         |
|------------------------------------|-----------------------------|---|-------|---|-------------------------|
|                                    |                             | Experimental                            | Calc. | Experimental  | Calculated              |
| 1b <sub>1</sub> → 3s <sub>a1</sub> | <sup>3</sup> B <sub>1</sub> | 7.2, b) 7.0 d)                          | 6.62  | 0.061, a) 0.041, i) 0.046 k)                          | 3.43 × 10 <sup>-3</sup> |
|                                    | <sup>1</sup> B <sub>1</sub> | 7.4, c,d) 7.49 e)                       | 7.37  |   |                         |
| 1b <sub>1</sub> → 3p <sub>b2</sub> | <sup>3</sup> A <sub>2</sub> | 9.1, b) 9.2, f) 8.9 d)                  | 9.29  |   |                         |
|                                    | <sup>1</sup> A <sub>2</sub> | 9.1 k)                                  | 9.56  |   |                         |
| 1b <sub>1</sub> → 3p <sub>a1</sub> | <sup>3</sup> B <sub>1</sub> | 9.98 d)                                 | 10.14 | (3400) l)   | 7.00 × 10 <sup>-4</sup> |
|                                    | <sup>1</sup> B <sub>1</sub> | 10.01, b,c,d,f,g) 9.996 e)              | 10.19 |   |                         |
| 1b <sub>1</sub> → 3p <sub>b1</sub> | <sup>3</sup> A <sub>1</sub> | 9.81, c) 9.80 d)                        | 9.93  | (4770) l)   | 1.31 × 10 <sup>-3</sup> |
|                                    | <sup>1</sup> A <sub>1</sub> | 10.14, g) 10.17, c) 10.172, e) 10.16 d) | 10.18 |   |                         |
| 1b <sub>1</sub> IP                 | <sup>2</sup> A <sub>1</sub> | 12.62 j)                                | 13.33 |   |                         |
| 3a <sub>1</sub> → 3s <sub>a1</sub> | <sup>3</sup> A <sub>1</sub> | 9.3 d)                                  | 9.16  | 0.05 i,k)   | 3.71 × 10 <sup>-3</sup> |
|                                    | <sup>1</sup> A <sub>1</sub> | 9.7, b,c,d,g) 9.73 e)                   | 9.98  |   |                         |
| 3a <sub>1</sub> → 3p <sub>b2</sub> | <sup>3</sup> B <sub>2</sub> |   | 11.47 |   | 1.05 × 10 <sup>-2</sup> |
|                                    | <sup>1</sup> B <sub>2</sub> |   | 11.81 |   |                         |
| 3a <sub>1</sub> → 3p <sub>a1</sub> | <sup>3</sup> A <sub>1</sub> |   | 12.03 |   | 2.55 × 10 <sup>-4</sup> |
|                                    | <sup>1</sup> A <sub>1</sub> |   | 12.32 |   |                         |
| 3a <sub>1</sub> → 3p <sub>b1</sub> | <sup>3</sup> B <sub>1</sub> |   | 12.16 |   | 9.84 × 10 <sup>-4</sup> |
|                                    | <sup>1</sup> B <sub>1</sub> | 11.91 g,h)                              | 12.20 |   |                         |
| 3a <sub>1</sub> IP                 | <sup>2</sup> A <sub>1</sub> | 14.68 j)                                | 14.71 |   |                         |

a) E.N. Lassette and A. Skerbele, J. Chem. Phys. 60 (1974) 2464.

b) Ref. [28].

c) Ref. [30].

d) Ref. [2].

e) J.W.C. Johns, Can. J. Phys. 41 (1963) 209.

f) G. Schula, J. Chem. Phys. 33 (1960) 1661.

g) A. Skeberle, M. Dillon and E.N. Lassette, J. Chem. Phys. 49 (1968) 5042.

h) K. Watanabe and A.S. Jursa, J. Chem. Phys. 41 (1964) 1650.

i) Ref. [27].

j) Ref. [4].

k) K. Watanabe and M. Zelikoff, J. Opt. Soc. Amer. 43 (1953) 753.

l) Ref. [7].

oxygen [1–4]. The results of our IVO calculations on H<sub>2</sub>O are compared with earlier IVO calculations in table 1. The previous calculations employed double zeta quality basis sets (augmented by various sets of diffuse functions), which are more flexible than the minimal basis set (augmented with diffuse functions) used in this work. The inflexibility of the minimal basis set introduces 0.1 to 0.2 eV errors except for the states involving excitation to the 3p<sub>b2</sub> orbital where 0.4 to 0.5 eV errors are encountered. Comparison of the present IVO calculations with the best values obtained from a consideration of both experiment and theory [1] reveals errors of 0.2 eV on the average. The transitions with the largest errors (0.6 eV for triplet 1b<sub>1</sub> →

3p<sub>b2</sub> and 0.4 eV for triplet 1b<sub>1</sub> → 3s) involve the orbitals exhibiting greater contraction (vide infra), presumably due to the extra amount of valence character in the wavefunction. For methanol only one orbital (3s) exhibits such extra contraction and hence only the 3s transition would be expected to have the large error (this is observed, vide infra). For dimethyl ether no transition should exhibit this effect (as observed).

In table 2 the calculated vertical excitation energies and oscillator strengths are compared with experiment. (Note well: Experimental molar extinction coefficient are listed parenthetically when oscillator strengths are not available.) The calculated oscillator strengths are much too small, but the relative magnitudes are in rough

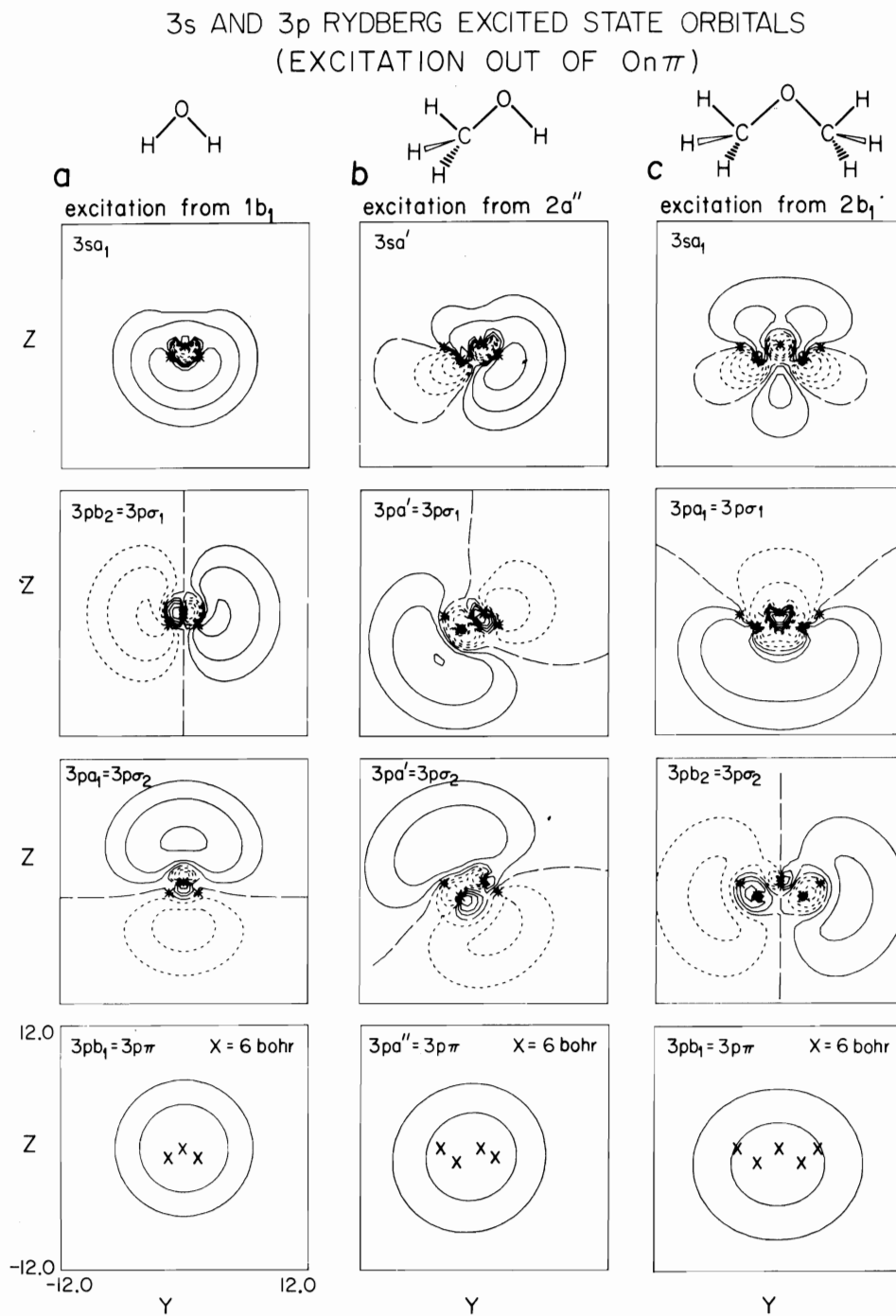


Fig. 1. Contour plots of the 3s and 3p Rydberg orbitals excited from the  $n\pi$  oxygen lone pair orbital of (a)  $H_2O$ , (b)  $CH_3OH$ , and (c)  $CH_3OCH_3$ . The plots are in the YZ plane except for the  $3p\pi$  orbitals which are plotted in the  $X = 6$  bohr plane. The contours are: 0.0,  $\pm 0.01$ ,  $\pm 0.02154$ ,  $\pm 0.04641$ ,  $\pm 0.1$ , etc. (that is, factors of 2.154).

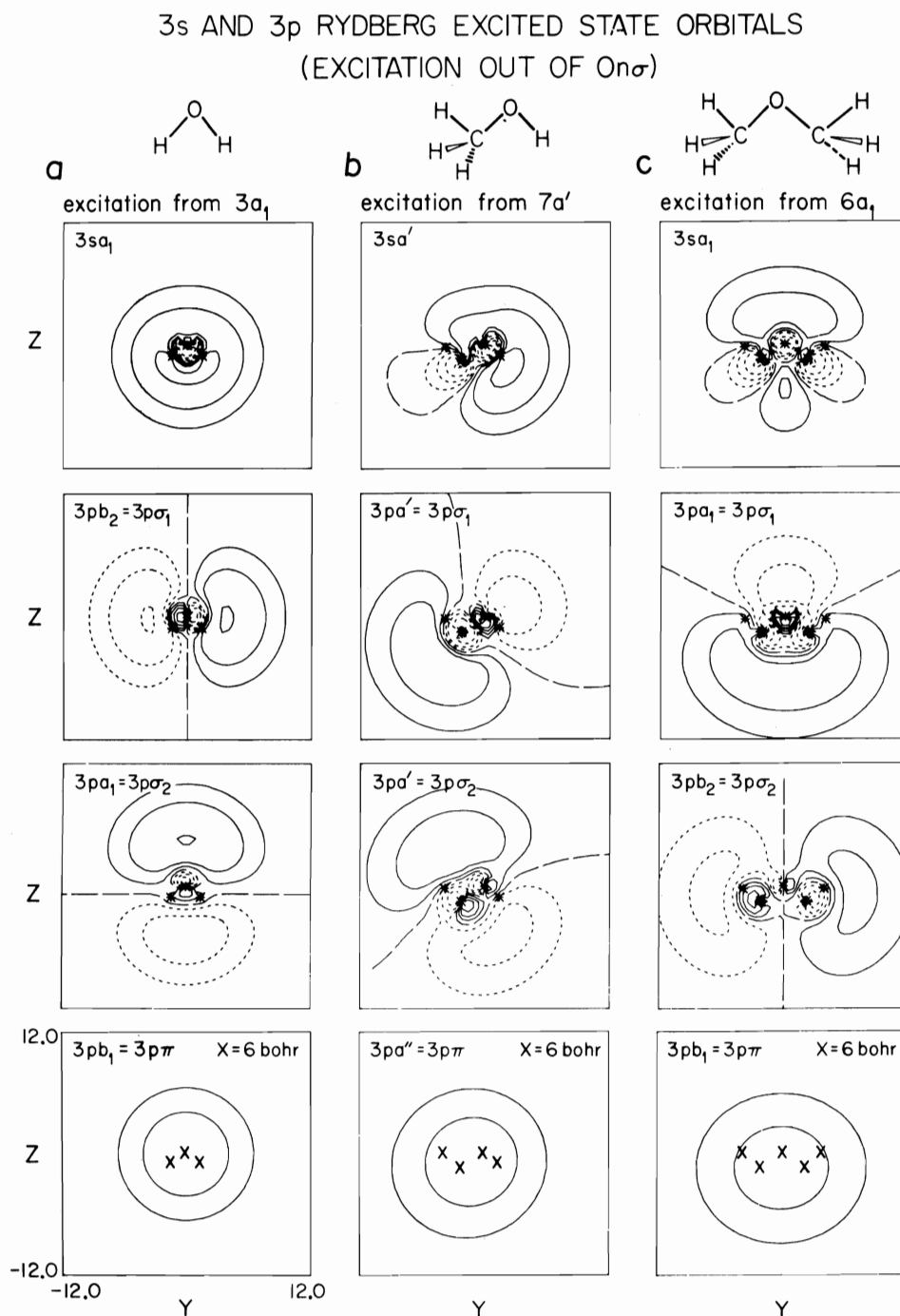


Fig. 2. Contour plots of the 3s and 3p Rydberg orbitals excited from the  $n\sigma$  oxygen lone pair orbital of (a)  $H_2O$ , (b)  $CH_3OH$ , and (c)  $CH_3OCH_3$ . The plots are in the YZ plane except for the  $3p_{\pi}$  orbitals which are plotted in the  $X = 6$  bohr plane. The contours are 0.0,  $\pm 0.01$ ,  $\pm 0.02154$ ,  $\pm 0.04641$ ,  $\pm 0.1$ , etc. (that is, factors of 2.154).

Table 3  
Sizes of Rydberg orbitals for water (bohr)<sup>a)</sup>

| Excitation                         | State                       | $\langle x^2 \rangle$ | $\langle y^2 \rangle$ | $\langle z^2 \rangle$ | $\sqrt{\langle r^2 \rangle}$ |
|------------------------------------|-----------------------------|-----------------------|-----------------------|-----------------------|------------------------------|
| 1b <sub>1</sub> → 3s <sub>a1</sub> | <sup>3</sup> B <sub>1</sub> | 5.077                 | 5.602                 | 6.300                 | 4.121                        |
|                                    | <sup>1</sup> B <sub>1</sub> | 6.484                 | 6.817                 | 7.836                 | 4.597                        |
| 1b <sub>1</sub> → 3p <sub>b2</sub> | <sup>3</sup> A <sub>2</sub> | 5.702                 | 17.333                | 5.851                 | 5.375                        |
|                                    | <sup>1</sup> A <sub>2</sub> | 6.595                 | 19.917                | 6.680                 | 5.761                        |
| 1b <sub>1</sub> → 3p <sub>a1</sub> | <sup>3</sup> B <sub>1</sub> | 8.502                 | 8.502                 | 22.498                | 6.285                        |
|                                    | <sup>1</sup> B <sub>1</sub> | 8.689                 | 8.689                 | 22.933                | 6.349                        |
| 1b <sub>1</sub> → 3p <sub>b1</sub> | <sup>3</sup> A <sub>1</sub> | 23.172                | 7.724                 | 7.724                 | 6.214                        |
|                                    | <sup>1</sup> A <sub>1</sub> | 26.351                | 8.784                 | 8.784                 | 6.627                        |
| 3a <sub>1</sub> → 3s <sub>a1</sub> | <sup>3</sup> A <sub>1</sub> | 5.879                 | 6.325                 | 7.103                 | 4.394                        |
|                                    | <sup>1</sup> A <sub>1</sub> | 7.769                 | 7.964                 | 8.518                 | 4.925                        |
| 3a <sub>1</sub> → 3p <sub>b2</sub> | <sup>3</sup> B <sub>2</sub> | 6.127                 | 18.574                | 6.253                 | 5.564                        |
|                                    | <sup>1</sup> B <sub>2</sub> | 7.303                 | 21.954                | 7.331                 | 6.049                        |
| 3a <sub>1</sub> → 3p <sub>a1</sub> | <sup>3</sup> A <sub>1</sub> | 8.143                 | 8.143                 | 21.606                | 6.156                        |
|                                    | <sup>1</sup> A <sub>1</sub> | 9.075                 | 9.075                 | 26.072                | 6.650                        |
| 3a <sub>1</sub> → 3p <sub>b1</sub> | <sup>3</sup> B <sub>1</sub> | 24.448                | 8.149                 | 8.149                 | 6.383                        |
|                                    | <sup>1</sup> B <sub>1</sub> | 24.922                | 8.307                 | 8.307                 | 6.445                        |

a) 1 bohr = 0.529177 Å.

agreement with experiment. The contour plots of the Rydberg orbitals in figs. 1a and 2a provide more insight into the nature and relative ordering of the low-lying excited states. The OH bonds in water are strongly polarized toward the oxygen. As a result, an electron in the 3s<sub>a1</sub> or 3p<sub>b2</sub> orbital "sees" partially unshielded protons; the 3s<sub>a1</sub> and 3p<sub>b2</sub> orbitals tighten and are stabilized relative to the other 3p orbitals. The shift toward the hydrogens is evident from the plots in figs. 1a and 2a, while the actual tightening of the orbitals is evident from the expectation values for  $\sqrt{\langle r^2 \rangle}$  listed in table 3. Although the 3s<sub>a1</sub> and 3p<sub>b2</sub> orbitals do contract significantly, they are still  $2\frac{1}{2}$  times larger than any of the valence orbitals (using  $\sqrt{\langle r^2 \rangle}$  as a measure of orbital size) and so warrant the appellation "Rydberg orbitals".

The 3p<sub>a1</sub> orbital shifts away from the hydrogens (cf. figs. 1a and 2a) in order to remain orthogonal to the 3s<sub>a1</sub> orbital, and hence it is not stabilized. The 3p<sub>b1</sub> orbital has a node passing through the hydrogens and so it too is not stabilized. Finally, the shift of the 3s<sub>a1</sub> and 3p<sub>b2</sub> orbitals toward the hydrogens is not as great when the excitation occurs out of the in-plane oxygen lone pair. The smaller shift arises simply from

the repulsive interactions induced by the Pauli principle between the singly-occupied Rydberg and the nσ orbitals. When the nσ orbital is doubly-occupied, as in the nπ → 3s, 3p states, the repulsion is much greater than when nσ is only singly-occupied as in the nσ → 3s, 3p states.

### 3.2. Methanol

Methylation of water destabilizes the oxygen lone pairs via repulsive pair-pair interactions. Consequently, the out-of-plane (nπ) and in-plane (nσ) lone pair ionization potentials decrease by 1.66 and 2.06 eV, respectively (cf. tables 2 and 4). On the other hand, the excited Rydberg 3s and 3p orbitals must be orthogonal to the electron pairs in the methyl group, which diminishes the stabilization (term values) of the 3s<sub>a1</sub> and 3p<sub>b2</sub> orbitals with respect to the values found in water. The net result is that the excitation energies in methanol are smaller by 0.5 to 1.5 eV relative to water (cf. tables 2 and 4).

The plots of the excited orbitals in figs. 1b and 2b clearly display the effect of the methyl group. The 3s<sub>a1</sub> orbital is shifted toward the remaining hydroxylic hydrogen. The 3s character is not very evident from the contour plot; however, the approximate equality of the expectation values for  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ , and  $\langle z^2 \rangle$  (cf. table 5) demonstrates the basically spherical nature of the orbital. The effect of methylation is also evident from the 9% increase in size of the 3s orbital relative to water. Finally, the stability (term value) of the 3s orbital has decreased by approximately 1 eV (cf. table 6).

The asymmetry of methanol forces the 3p<sub>b2</sub> and 3p<sub>a1</sub> orbitals of water to come into contact with the result that the 3p<sub>b2</sub> orbital (i.e., 3pσ<sub>1</sub>) mixes in a significant amount of 3p<sub>a1</sub> character to retain its favorable interactions with the remaining hydroxylic hydrogen (cf. figs. 1b and 2b, second row). As a result, the stability of the 3p<sub>b2</sub> orbital (denoted by 3pσ<sub>1</sub> in table 6) decreases by only 0.2 to 0.3 eV in methanol. The stability of the 3p<sub>a1</sub> orbital (denoted by 3pσ<sub>2</sub> in table 6), which is not stabilized in H<sub>2</sub>O, decreases by 0.1 eV in methanol. Finally, the stability of the 3p<sub>b1</sub> orbital (denoted by 3pπ in table 6) decreases by a comparable amount (0.1 eV) as expected from its nodal plane through the carbon, oxygen, and hydroxylic hydrogen.

We turn now to the assignment of the experimental spectra of methanol. A broad weak band has been

Table 4  
Low-lying excited states of methanol

| Excitation   | State            | Vertical excitation energy (eV) |            | Oscillator strength (molar extinction coefficient) |                         |
|--------------|------------------|---------------------------------|------------|--|-------------------------|
|              |                  | Experimental                    | Calculated | Experimental                                       | Calculated              |
| 2a'' → 3sa'  | <sup>3</sup> A'' | 6.50 a)                         | 6.23       | 0.005 c)   | 1.96 × 10 <sup>-3</sup> |
|              | <sup>1</sup> A'' | 6.69, b) 6.74 c,d)              | 6.72       |  |                         |
| 2a'' → 3pa'  | <sup>3</sup> A'' | 7.80 b)                         | 7.90       | (3440) e)  | 3.67 × 10 <sup>-3</sup> |
|              | <sup>1</sup> A'' |                                 | 8.20       |  |                         |
| 2a'' → 3pa'  | <sup>3</sup> A'' |                                 | 8.56       |  | 3.91 × 10 <sup>-6</sup> |
|              | <sup>1</sup> A'' |                                 | 8.60       |  |                         |
| 2a'' → 3pa'' | <sup>3</sup> A'  | 8.41 b)                         | 8.53       | (3420) e)  | 8.33 × 10 <sup>-4</sup> |
|              | <sup>1</sup> A'  |                                 | 8.63       |  |                         |
| 2a'' IP      | <sup>2</sup> A'' | 10.96 d)                        | 12.11      |  |                         |
| 7a' → 3sa'   | <sup>3</sup> A'  |                                 | 8.22       |  | 1.37 × 10 <sup>-3</sup> |
|              | <sup>1</sup> A'  |                                 | 8.71       |  |                         |
| 7a' → 3pa'   | <sup>3</sup> A'  | 9.44 b)                         | 9.66       |  | 1.81 × 10 <sup>-2</sup> |
|              | <sup>1</sup> A'  |                                 | 9.99       |  |                         |
| 7a' → 3pa'   | <sup>3</sup> A'  |                                 | 10.10      |  | 6.15 × 10 <sup>-3</sup> |
|              | <sup>1</sup> A'  |                                 | 10.20      |  |                         |
| 7a' → 3pa''  | <sup>3</sup> A'' |                                 | 10.28      |  | 5.78 × 10 <sup>-4</sup> |
|              | <sup>1</sup> A'' |                                 | 10.30      |  |                         |
| 7a' IP       | <sup>2</sup> A'  | 12.62 d)                        | 13.41      |  |                         |

a) Ref. [28]. b) Ref. [26]. c) Ref. [27]. d) Ref. [5]. e) Ref. [7].

observed at 6.7 eV [7] in both optical and electron impact spectra. Early assignments ascribed the feature to various types of valence transitions [23–25], while more recent work ascribes the band to the <sup>1</sup>A'' (2a'' → 3sa') state [5,7,26]. The latter assignment is supported by our IVO calculations, which predict an excitation energy of 6.72 eV, in excellent agreement with the experimental result of 6.74 eV [5,27].

At higher energies there are two strong, structured bands (7.80 and 8.41 eV) which have most recently been assigned to <sup>1</sup>(2a'' → 3p) transitions [7,26]. The IVO calculations predict <sup>1</sup>(2a'' → 3p) transitions at 8.20, 8.60, and 8.63 eV. The state at 8.20 eV, <sup>1</sup>A'' (2a'' → 3pa'), corresponds to the <sup>1</sup>A<sub>2</sub> (1b<sub>1</sub> → 3pb<sub>2</sub>) state in water, whose energy was overestimated by 0.4 eV (cf. table 2). Therefore it is reasonable to assign the 7.80 eV transition to the <sup>1</sup>A'' (2a'' → 3pa') state calculated at 8.20 eV. Next we note that the oscillator strength for the other <sup>1</sup>(2a'' → 3pa') transition is more

than two orders of magnitude smaller than that for the <sup>1</sup>(2a'' → 3pa'') transition. Acknowledging the evident crudeness of the calculated oscillator strengths, the calculations still warrant assigning the 8.41 eV feature to the <sup>1</sup>A' (2a'' → 3pa'') state.

The 3.16 eV term value (stability) for the first <sup>1</sup>A'' (2a'' → 3pa') state has been considered anomalously large [7,26], the expected value being 2.6 eV. However, the origin of this apparent anomaly may be readily explained. Until the recent electron impact [2] and high quality theoretical work on water [1,4], the position of the dipole forbidden <sup>1</sup>A<sub>2</sub> (1b<sub>1</sub> → 3pb<sub>2</sub>) state was unknown. As discussed previously, the 3pb<sub>2</sub> orbital is stabilized by ~0.9 eV relative to the other two 3p orbitals due to favorable interactions with the electron-deficient hydrogens. As a consequence, the term value of the 3pb<sub>2</sub> orbital is 3.4 eV compared with 2.45 and 2.62 eV for the other 3p orbitals. Upon methylation the term values for all the orbitals decrease slightly,

Table 5  
Sizes of Rydberg orbitals for methanol (bohr)

| Excitation              | State   | $\langle x^2 \rangle$ | $\langle y^2 \rangle$ a) | $\langle z^2 \rangle$ a) | $\sqrt{\langle r^2 \rangle}$ |
|-------------------------|---------|-----------------------|--------------------------|--------------------------|------------------------------|
| $2a'' \rightarrow 3sa'$ | $^3A''$ | 6.346                 | 7.024                    | 6.657                    | 4.475                        |
|                         | $^1A''$ | 8.506                 | 7.918                    | 8.702                    | 5.103                        |
| $2a'' \rightarrow 3pa'$ | $^3A''$ | 10.473                | 18.156                   | 22.163                   | 7.127                        |
|                         | $^1A''$ | 11.423                | 23.832                   | 23.690                   | 7.678                        |
| $\rightarrow 3pa'$      | $^3A''$ | 11.535                | 22.766                   | 19.720                   | 7.350                        |
|                         | $^1A''$ | 11.630                | 21.251                   | 23.082                   | 7.481                        |
| $\rightarrow 3pa''$     | $^3A'$  | 31.587                | 12.754                   | 11.521                   | 7.474                        |
|                         | $^1A'$  | 33.686                | 13.588                   | 12.289                   | 7.718                        |
| $7a' \rightarrow 3sa'$  | $^3A'$  | 7.349                 | 7.539                    | 7.504                    | 4.732                        |
|                         | $^1A'$  | 10.291                | 8.896                    | 9.945                    | 5.397                        |
| $7a' \rightarrow 3pa'$  | $^3A'$  | 10.619                | 22.072                   | 20.420                   | 7.288                        |
|                         | $^1A'$  | 11.397                | 27.539                   | 22.051                   | 7.809                        |
| $\rightarrow 3pa'$      | $^3A'$  | 10.623                | 19.211                   | 21.739                   | 7.181                        |
|                         | $^1A'$  | 11.090                | 20.573                   | 24.013                   | 7.462                        |
| $\rightarrow 3pa''$     | $^3A''$ | 32.796                | 13.403                   | 12.044                   | 7.632                        |
|                         | $^1A''$ | 33.191                | 13.526                   | 12.171                   | 7.674                        |

a) Note that  $\langle yz \rangle \neq 0$  for methanol.

but now the strongest optical transitions in methanol correspond to the  $^1A_2$  and  $^1A_1$  states of water (rather than  $^1B_1$  and  $^1A_1$ ). Previous workers had assumed that the two transitions observed optically in water and methanol correspond to one another [7]. This is not the case and the problem of the anomalously large term value disappears.

Assignment of higher lying transitions on the basis of the present IVO calculations is more difficult since  $^1(2a'' \rightarrow 3d, 4s, \text{ or } 4p)$  transitions, which were not calculated, occur in the same spectral region as the calculated  $^1(7a' \rightarrow 3s, 3p)$  transitions. IVO calculations with a more flexible basis that properly describes the 3d, 4s, and 4p Rydberg orbitals are needed to elucidate this portion of the spectrum. Tam and Brion [26] have assigned a feature at 9.44 eV to a  $7a' \rightarrow 3p$  transition. The calculated  $7a' \rightarrow 3p$  transition is at 9.99 eV. However, this transition involves the stabilized  $3pa'$  Rydberg orbital. The other IVO calculations on states involving this orbital have overestimated the energy by 0.4 eV. Therefore, the calculations appear to support the assignment of Tam and Brion [26] and indicate that the state symmetry is  $^1A'$  ( $7a' \rightarrow 3pa'$ ).

Using electron impact spectroscopy, Knoop et al.

Table 6  
Stabilities (term values) of the excited Rydberg orbitals for water, methanol, and dimethyl ether (eV). ( $n\sigma$  denotes the in-plane oxygen lone pair orbital;  $n\pi$  denotes the out-of-plane oxygen lone pair orbital.) Experimental values are listed parenthetically

| Excitation                           | H <sub>2</sub> O <sup>a)</sup> | CH <sub>3</sub> OH          | CH <sub>3</sub> OCH <sub>3</sub> |
|--------------------------------------|--------------------------------|-----------------------------|----------------------------------|
| $^3(n\pi \rightarrow 3s)$            | 6.00 (5.46)                    | 4.73 (4.46) <sup>b)</sup>   | 3.73                             |
| $^3(n\sigma \rightarrow 3s)$         | 5.25 (5.33)                    | 4.40                        | 3.52                             |
| $^1(n\pi \rightarrow 3s)$            | 5.25 (5.13)                    | 4.24 (4.22) <sup>c,d)</sup> | 3.28 (3.29) <sup>c,f)</sup>      |
| $^1(n\sigma \rightarrow 3s)$         | 4.70 (4.95)                    | 3.91                        | 3.20 (3.45) <sup>e)</sup>        |
| $^3(n\pi \rightarrow 3p\pi)$         | 2.69 (2.81)                    | 2.43                        | 2.32                             |
| $^3(n\sigma \rightarrow 3p\pi)$      | 2.52 (2.82)                    | 2.33                        | 2.23                             |
| $^1(n\pi \rightarrow 3p\pi)$         | 2.44 (2.45)                    | 2.34 (2.55) <sup>e)</sup>   | 2.25 (2.39) <sup>c,e)</sup>      |
| $^1(n\sigma \rightarrow 3p\pi)$      | 2.48 (2.77)                    | 2.32                        | 2.21                             |
| $^3(n\pi \rightarrow 3p\sigma_1)$    | 3.33 (3.5)                     | 3.06                        | 3.03                             |
| $^3(n\sigma \rightarrow 3p\sigma_1)$ | 3.21 (3.6)                     | 2.96                        | 2.88                             |
| $^1(n\pi \rightarrow 3p\sigma_1)$    | 3.06 (3.4)                     | 2.76 (3.16) <sup>e)</sup>   | 2.66 (2.70) <sup>e)</sup>        |
| $^1(n\sigma \rightarrow 3p\sigma_1)$ | 2.87 (3.2)                     | 2.63 (3.18) <sup>e)</sup>   | 2.48 (2.71) <sup>e)</sup>        |
| $^3(n\pi \rightarrow 3p\sigma_2)$    | 2.48 (2.7)                     | 2.40                        | 2.20                             |
| $^3(n\sigma \rightarrow 3p\sigma_2)$ | 2.65 (2.9)                     | 2.52                        | 2.21                             |
| $^1(n\pi \rightarrow 3p\sigma_2)$    | 2.43 (2.62)                    | 2.36                        | 2.15                             |
| $^1(n\sigma \rightarrow 3p\sigma_2)$ | 2.36 (2.6)                     | 2.42                        | 2.15                             |

a) Experimental values from ref. [1].

b) Ref. [28].

c) Ref. [27].

d) Ref. [5].

e) Ref. [26].

f) Ref. [34].

[28] have observed a weak band at 4.3 eV, which they assigned to a low-lying triplet state. Our calculations contradict this assignment, since the lowest triplet state ( $n\pi \rightarrow 3sa'$ ) is predicted to be at 6.2 eV. In fact, Knoop et al. [28] have tentatively identified another triplet state at 6.5 eV, which we assign as  $n\pi \rightarrow 3sa'$  (in water the corresponding transition was underestimated by  $\sim 0.5$  eV for IVO). As to the 4.3 eV "triplet", a similar feature was observed in water at 4.5 eV by Knoop et al. [28] and other workers [2,29,30]. This broad weak band is unidentified but may arise from water dimers [4,31,32]. The analogy to water reinforces the conclusion that the 4.3 eV feature does not correspond to a vertical excited triplet state in the methanol monomer.

Recently Snyder and Johnson [33] have shown that the observed circular dichroism (CD) of the first three transitions in 2-butanol is consistent with  $n \rightarrow \sigma_{OH}^*$ ,  $n \rightarrow \sigma_{CO}^*$ , and  $n \rightarrow 3s_O$  transitions. These calculations are probably consistent with our results on CH<sub>3</sub>OH even



though the orbitals are in fact Rydberg-like. Our  $3sa'$  orbital (first transition) is oriented along the OH axis and antibonding along the OH bond, as assumed in the CD calculations, while our  $3p\sigma_1$  orbital (second transition) is oriented along the CO axis and antibonding along the CO bond, as assumed in the CD calculations. The third transition is, of course, not  $n \rightarrow 3s_O$  as assumed in the CD calculations but perhaps the CD spectrum could also be explained as  $n\pi \rightarrow 3p\pi$ . In addition, there is the second  $n\pi \rightarrow 3p\sigma$  transition which is essentially forbidden for methanol but which may become more allowed for larger alcohols.

### 3.3. Dimethyl ether

The effects of methylation observed in methanol are basically the same in dimethyl ether. The presence of two methyl groups further destabilizes the oxygen lone pairs so that the out-of-plane and in-plane lone

pair ionization potentials decrease by 0.92 and 0.71 eV, respectively (cf. tables 4 and 7). Similarly, the extra stabilization of the  $3sa'$  and  $3pa'$  orbitals arising from the hydroxylic hydrogen is destroyed (cf. table 6). The calculated vertical excitations energies and oscillator strengths are listed in table 7 and compared with experiment.

The contour plots in figs. 1c and 2c of the excited Rydberg orbitals for dimethyl ether manifest the distortions brought on by the presence of the methyl groups. Comparison of the values for  $\sqrt{\langle r^2 \rangle}$  in tables 3, 5, and 7 reveals a significant increase in the size of the orbitals for the series water, methanol, and dimethyl ether. However, the plots in figs. 1c and 2c and expectation values in table 8 attest to the fact that the orbitals remain basically 3s or 3p Rydberg in character.

The stabilities of the Rydberg orbitals decrease as a result of methylation of water and methanol (cf. table 6). The 3s orbital, which derived the greatest bene-

Table 7  
Low-lying excited states of dimethyl ether

| Excitation               | State   | Vertical excitation energy (eV) |            | Oscillator strength |                       |
|--------------------------|---------|---------------------------------|------------|---------------------|-----------------------|
|                          |         | Experimental                    | Calculated | Experimental        | Calculated            |
| $2b_1 \rightarrow 3sa_1$ | $^3B_1$ | 6.67, a) 6.75 b,c)              | 6.31       | 0.035 b)            | $1.48 \times 10^{-2}$ |
|                          | $^1B_1$ |                                 | 6.76       |                     |                       |
| $2b_1 \rightarrow 3pb_2$ | $^3A_2$ |                                 | 7.84       |                     |                       |
|                          | $^1A_2$ |                                 | 7.89       |                     |                       |
| $\rightarrow 3pa_1$      | $^3B_1$ | 7.34 a)                         | 7.01       |                     | $2.35 \times 10^{-4}$ |
|                          | $^1B_1$ |                                 | 7.38       |                     |                       |
| $\rightarrow 3pb_1$      | $^3A_1$ | 7.63, a,b) 7.65 c)              | 7.72       | 0.056 b)            | $1.73 \times 10^{-3}$ |
|                          | $^1A_1$ |                                 | 7.79       |                     |                       |
| $2b_1$ IP                | $^2B_1$ | 10.04 d)                        | 11.51      |                     |                       |
| $6a_1 \rightarrow 3sa_1$ | $^3A_1$ | (8.46) a)                       | 8.39       |                     | $1.56 \times 10^{-3}$ |
|                          | $^1A_1$ |                                 | 8.71       |                     |                       |
| $6a_1 \rightarrow 3pb_2$ | $^3B_2$ |                                 | 9.70       |                     | $5.30 \times 10^{-4}$ |
|                          | $^1B_2$ |                                 | 9.76       |                     |                       |
| $\rightarrow 3pa_1$      | $^3A_1$ | 9.20 a)                         | 9.03       |                     | $1.74 \times 10^{-2}$ |
|                          | $^1A_1$ |                                 | 9.43       |                     |                       |
| $\rightarrow 3pb_1$      | $^3B_1$ |                                 | 9.68       |                     |                       |
|                          | $^1B_1$ |                                 | 9.70       |                     |                       |
| $6a_1$ IP                | $^2A_1$ | 11.91 c)                        | 12.74      |                     | $2.36 \times 10^{-3}$ |

a) Ref. [26]. b) Ref. [27]. c) Ref. [34]. d) S. Cradock and R.A. Whiteford, J.C.S. Faraday II (1972) 281.

Table 8  
Sizes of Rydberg orbitals for dimethyl ether (bohr)

| Excitation               | State   | $\langle x^2 \rangle$ | $\langle y^2 \rangle$ | $\langle z^2 \rangle$ | $\sqrt{\langle r^2 \rangle}$ |
|--------------------------|---------|-----------------------|-----------------------|-----------------------|------------------------------|
| $2b_1 \rightarrow 3sa_1$ | $^3B_1$ | 8.257                 | 6.794                 | 6.041                 | 4.593                        |
|                          | $^1B_1$ | 16.030                | 8.432                 | 11.403                | 5.989                        |
| $2b_1 \rightarrow 3pb_2$ | $^3A_2$ | 13.801                | 43.798                | 16.764                | 7.589                        |
|                          | $^1A_2$ | 14.517                | 45.799                | 16.451                | 8.762                        |
| $\rightarrow 3pa_1$      | $^3B_1$ | 13.064                | 17.419                | 23.671                | 7.359                        |
|                          | $^1B_1$ | 8.819                 | 18.783                | 28.183                | 7.469                        |
| $\rightarrow 3pb_1$      | $^3A_1$ | 36.402                | 14.948                | 14.422                | 8.110                        |
|                          | $^1A_1$ | 37.706                | 15.229                | 14.772                | 8.228                        |
| $6a_1 \rightarrow 3sa_1$ | $^3A_1$ | 10.445                | 7.108                 | 7.769                 | 5.032                        |
|                          | $^1A_1$ | 16.185                | 9.944                 | 11.870                | 6.164                        |
| $6a_1 \rightarrow 3pb_2$ | $^3B_2$ | 13.660                | 44.539                | 14.930                | 8.552                        |
|                          | $^1B_1$ | 14.623                | 46.901                | 14.856                | 8.682                        |
| $\rightarrow 3pa_1$      | $^3A_1$ | 11.256                | 19.881                | 23.557                | 7.396                        |
|                          | $^1A_1$ | 10.666                | 18.637                | 34.115                | 7.964                        |
| $\rightarrow 3pb_1$      | $^3B_1$ | 37.180                | 15.054                | 14.582                | 8.174                        |
|                          | $^1B_1$ | 37.606                | 15.131                | 14.680                | 8.211                        |

fit from the hydroxylic hydrogens, is destabilized the most by methylation:  $\sim 1$  eV decrease per methyl group. On the other hand, the out-of-plane  $3p$  orbital ( $3p\pi$ ) is only mildly affected because of its nodal structure:  $\sim 0.15$  eV decrease per methyl group. The two in-plane  $3p$  orbitals behave differently as one ( $3p\sigma_1$ ) is stabilized by the hydroxylic hydrogen and the other ( $3p\sigma_2$ ) is not. As a consequence, the stability of  $3p\sigma_1$  decreases by 0.35 eV per methyl group, while that of  $3p\sigma_2$  decreases by only 0.15 eV. Moreover, the  $3pb_2$  orbital which was the most stable orbital in water ( $3p\sigma_1$ ) is the least stable in dimethyl ether ( $3p\sigma_2$ ) because of the orientation of the methyl groups approximately along the  $y$ -axis.

The IVO calculations predict the lowest excited singlet state,  $^1B_1$  ( $2b_1 \rightarrow 3sa_1$ ), to occur at 6.76 eV, in excellent agreement with the optical [27,34] and electron impact [26] spectra. The next set of transitions occurs at 7.34 [26] and 7.65 eV [34], both of which have been assigned to  $^1(2b_1 \rightarrow 3p)$  transitions [5,26]. The two bands are quite different, the 7.34 eV feature being broad, structureless, and weak compared with the strong structured band at 7.65 eV. This difference has led McDiarmid [6] to assign the 7.34 eV

band to a valence state (involving a one-electron promotion to an anti-bonding orbital) rather than a Rydberg state. The IVO calculations predict  $^1(2b_1 \rightarrow 3p)$  dipole-allowed transitions at 7.38 ( $n\pi \rightarrow 3pa_1$ ) and 7.79 eV ( $n\pi \rightarrow 3pb_1$ ) (cf. table 7), in good agreement with experiment. [The dipole-forbidden transition to the  $^1A_2$  ( $2b_1 \rightarrow 3pb_2$ ) is calculated at 7.38 eV.] Therefore, our calculations contravene the assignment of the 7.34 eV band to a valence state.

A broad weak band near 5.3 eV has been occasionally mentioned [6,35]. Our calculations indicate no vertical excitation of  $O(CH_3)_2$  in this region and further checking of the literature uncovered only a brief one-line mention in a 1935 paper [36].

It should be pointed out that the IVO method does not enforce all the excited states to be Rydberg in character. For example, a comparable basis set was used in IVO calculations of the excitation energies in pyrazine [37] considering promotions out of two highest occupied orbitals,  $6a_1$  ( $n$ ) and  $1b_{1g}$  ( $\pi$ ). The lowest excited states in the IVO calculations were found to involve  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitations, with excitations to Rydberg orbitals occurring at higher energies.

On the basis of term values, Tam and Brion [26] have assigned the band at 8.46 eV to either  $^1(2b_1 \rightarrow 3d)$  or  $^1(6a_1 \rightarrow 3s)$  and the band at 9.20 eV to  $^1(6a_1 \rightarrow 3p)$ . The 8.46 eV band has also been assigned to  $^1(2b_1 \rightarrow 4s)$  by McDiarmid [38] on the basis of its quantum defect and vibronic structure. The calculated energy for the  $^1(6a_1 \rightarrow 3s)$  transition is 8.71 eV and the energies for the dipole-allowed  $^1(6a_1 \rightarrow 3p)$  transitions are 9.43 and 9.76 eV. Since the calculated value for the analogous  $^1(3a_1 \rightarrow 3s)$  transition in water was too high by 0.25 eV, the calculations tend to support the assignment of the 8.46 eV band to  $^1(6a_1 \rightarrow 3s)$ . However, calculations on the  $^1(2b_1 \rightarrow 3d)$  and  $^1(2b_1 \rightarrow 4s)$  transitions are needed before a definite assignment may be made. Finally, we tentatively assign the 9.20 eV band to the  $^1A_1$  ( $6a_1 \rightarrow 3pa_1$ ) state calculated at 9.43 eV.

#### 4. Conclusion

Simple IVO calculations allow the assignments of the spectra of simple alcohols and ethers and provide some insight into the character of the excited states.

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