A complete active space self-consistent field multireference configuration interaction study of the low-lying excited states of BrO

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(Received 20 January 1999; accepted 24 August 2000)

A theoretical study of the excited states of the BrO radical has been carried out for the first time using high level ab initio molecular orbital methods. The vertical excitation energies for the low-lying excited states ($2^2\Pi$, $1^2\Sigma^+$, $1^2\Sigma^-$ and $1^2\Delta$) are calculated using the internally contracted multireference configuration interaction (MRCI) method. Based on vertical excitation energies, the ordering of the first few excited states are determined to be $2^2\Pi$, $1^2\Delta$, $1^2\Sigma^-$, and $1^2\Sigma^+$. The potential energy curves for the ground state ($X^2\Pi$) and several low-lying excited states are examined at the MRCI+Q/aug-cc-pVQZ level of theory. Several excited states are calculated to intersect the $2^2\Pi$ state, resulting in predissociation into Br$(2P)$+O($3P$). Results for the quartet states of BrO are also included, as well as calculations of the effects of spin–orbit coupling on the electronic states of BrO. © 2000 American Institute of Physics. [S0021-9606(00)31243-0]

I. INTRODUCTION

It is well known that BrO plays a significant role in the stratospheric catalytic destruction of O$_3$ via

Br+O$_3$→BrO+O$_2$,
BrO+O→Br+O$_2$,
Net:O+O$_3$→2O$_2$.

Additionally, BrO couples with ClO to participate in the catalytic destruction of O$_3$ via

Br+O$_3$→BrO+O$_2$,
Cl+O$_3$→ClO+O$_2$,
BrO+ClO→Br+Cl+O$_2$.
Net:2O$_3$→2O$_2$.

The second catalytic reaction cycle accounts for as much as 30% of the halogen-controlled loss of stratospheric ozone over Antarctica. In light of its great importance for the atmosphere, BrO has been the focus of various experimental work. However, surprisingly, only a small amount of theoretical work has addressed the ground state of BrO.

The BrO radical has a $2^2\Pi$ ground state, which has been thoroughly investigated experimentally by microwave, infrared, laser magnetic resonance, and electron spin resonance techniques. An accurate equilibrium rotational constant, bond length, vibrational frequency, and spin–orbit splitting constant are known. Most recently, Francisco et al. performed ab initio calculations on the ground state of the BrO radical, its cation, and its anion. In their work, several electron correlation methods, including second-order Möller–Plesset, fourth-order Möller–Plesset, configuration interaction single double, and coupled cluster single double triple were used with three kinds of basis sets, namely 6-311G(2df), triple zeta double polarized (TZ2P), and atomic natural orbital sets.

For the BrO radical, the high-lying excited states, $E^2\Sigma$ ($T_e = 64.916$ cm$^{-1}$), $F^2\Sigma$ ($T_e = 67.420$ cm$^{-1}$), and $G^2\Sigma$ ($T_e = 70.441$ cm$^{-1}$), had been observed by Duignan and Hudson by a three-photon resonantly enhanced multiphoton ionization detection scheme at wavelengths between 417 and 474 nm. Recently, Delmdahl et al. found another high-lying excited state around 56 000 cm$^{-1}$ using state-resolved two-photon laser induced fluorescence spectroscopy. Except for these studies, most of the attention has been focused on the first excited state, the $A^2\Pi$, of the BrO radical. The $X^2\Pi$→$A^2\Pi$ absorption spectrum of BrO, extensively studied and found to be in the 280–380 nm region with the strongest absorption feature around 338 nm, shows diffuse vibrational structure, which indicates predissociation. This 338 nm absorption feature has been often used to measure BrO in the atmosphere and in the laboratory. However, very little is known about the predissociation mechanism occurring throughout the $2^2\Pi$ (generally denoted as the $A^2\Pi$) state. Ab initio methods have been demonstrated to be an important tool in studying photochemistry phenomena, and have been extensively applied to many very important species of interstellar clouds. In this work, we have investigated several low-lying excited states of BrO using high level ab initio methods, such as complete active space self-consistent field (CASSCF) and internally contracted multimference configuration interaction (MRCI).

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II. COMPUTATIONAL METHODS

Initially the ground state ($X^1\Pi$) of BrO was optimized at both the UCCSD(T)\(^{17}\) and internally contracted MRCI\(^{18,19}\) levels of theory with the cc-pVTZ basis set of Dunning and co-workers\(^{20,21}\) and a TZ2P(2SP) basis set. The TZ2P(2SP) is a triple-zeta double polarized (TZ2P) basis set with two sets of sp diffuse functions in a segmented contraction scheme. The generally contracted cc-pVTZ basis set consists of a [6s5p3d1f] contraction on the Br atom\(^{22}\) and [4s3p2d1f] on the O atom.\(^{20}\) The oxygen TZ2P basis set is comprised of Dunning’s\(^{23}\) 5s3p contraction with 2 d-type polarization functions taken from Dunning.\(^{20}\) The Br TZ2P basis set is composed of a 6s5p2d contraction of a 17s13p6d primitive set given by Schaefer, Huber, and Ahlrichs.\(^{23}\) The exponents for the sp diffuse functions were determined using a procedure described in Ref. 24. The resulting exponent values for the first set were 0.0896 and 0.0583 (s and p, respectively) for Or and 0.0500 and 0.0391 (s and p) for Br. The second set were 0.0305 and 0.0203 for O and 0.0165 and 0.0148 for Br. In contrast to the cc-pVTZ set, the TZ2P(2SP) basis set did not contain any f functions.

Employing these two basis sets, the vertical excitation energies for the first four excited states (2 $^1\Pi$, 1 $^3\Delta$, 1 $^3\Sigma^-$, and 1 $^3\Sigma^+$) were calculated at the MRCI level using the MRCI optimized bond length of the ground state. These calculations were based on molecular orbitals (MOs) obtained in state-averaged CASSCF\(^{25,26}\) calculations with equal weights for all states. The active space used for these calculations consisted of 13 electrons in 11 MOs, i.e., the highest four valence MOs of $a_1$, and two valence MOs of $b_1$ and $b_2$ symmetry, as well as the lowest nonvalence virtual MO of $a_1$, $b_1$, and $b_2$ symmetry. The size of the resulting CAS was 19 234 CSFs (configuration state functions) for the $A_1$ states, 19 070 CSFs for the $B_1$ and $B_2$ states, and 18 856 CSFs for the $A_2$ state. The core molecular orbitals (8 $\times$ $a_1$, 3 $\times$ $b_1$, 3 $\times$ $b_2$, and 1 $\times$ $a_2$) were constrained to be doubly occupied but fully optimized. The reference function for the subsequent MRCI calculations employed the same active space as in the CASSCF. With the TZ2P(2SP) basis set, the number of variational parameters in the MRCI after internal contraction was 2 306 338 for the $A_1$ state, 2 032 786 for the $B_1$ and $B_2$ states, and 2 299 529 for the $A_2$ state. The sizes of the resulting MRCI calculations were slightly smaller with the cc-pVTZ basis set. Only the valence electrons were correlated. In all the calculations, the $C_{2v}$ point group was used throughout.

Potential energy curves from $r = 2.95$ to 6.05 bohr were calculated for a total of ten doublet states (2 $^3\Sigma^+$, 4 $^3\Pi$, 2 $^3\Delta$, 2 $^3\Sigma^-$) and six quartet states (2 $^3\Sigma^+$, 2 $^3\Pi$, 2 $^3\Delta$, 2 $^3\Sigma^-$, and 2 $^3\Phi$) of BrO using MRCI wave functions and the standard aug-cc-pVTZ basis set. Six of the doublet states and the corresponding quartets comprise all of the electronic states that correlate with ground state atomic products, Br($^2P$) and O($^3P$). The other four doublet states are a subset of the nine states that correlate to the low-lying $^1D$ excited state of oxygen atom (states of $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^2\Sigma^-$, and $^2\Phi$ symmetry have been excluded). For these calculations a smaller, full valence active space was used (thirteen electrons in eight orbitals) for the CASSCF and subsequent MRCI calculations, which corresponded to, for example, 42 CSFs for the $^3\Pi$ states and 14 CSFs for the $^3\Phi$ states. With these reference functions, the resulting sizes of the MRCI calculations typically involved about 750 000 variational parameters for the doublet states and about 400 000 for the quartets. In contrast to the calculations of the vertical excitation energies discussed previously, orbitals used in the MRCI calculations of the potential curves were obtained by a state average (equal weights) of only those states within the same $\Sigma$ or $\Sigma^+$ symmetry. For instance, the orbitals for the calculations on the $^3\Pi$ states were obtained from CASSCF calculations involving only four states each of $b_1$ and $b_2$ symmetry. In each case, the multireference analog of the Davidson correction\(^{25}\) was included for the approximate treatment of higher excitations (MRCI+$Q$).

In order to ascertain the impact of spin–orbit (SO) coupling on the electronic states of BrO, SO calculations were carried out within the interacting states method. Using a segmented contraction version of the cc-pVTZ basis set\(^{28}\) with diffuse sp functions from the standard aug-cc-pVTZ set, SO matrix elements were calculated at the MRCI level of theory (valence electrons correlated only) with the one- and two-electron Breit–Pauli operator as implemented in the MOLPRO program.\(^{29}\) The spin–orbit eigenstates were obtained by diagonalization of $H_{el} + H_{SO}$ in a basis of eigenfunctions of $H_{el}$. All sixteen electronic states described previously (ten doublets and six quartets) were included in the SO calculations, and the diagonal elements of $H_{el} + H_{SO}$ were replaced by their MRCI+$Q$/aug-cc-pVQZ values described previously. Additionally, in the calculation of the SO matrix elements, state averaged orbitals were used with equal weights for all states in order to obtain a common set of MOs.

The UCCSD(T) geometry optimization was carried out with the GAUSSIAN 94 program,\(^{30}\) while all of the CASSCF and internally contracted MRCI calculations have been performed using the MOLPRO 96 and 2000 suite of programs.\(^{31}\)

III. RESULTS AND DISCUSSION

A. Ground state of BrO

Table I lists the optimized bond lengths of the BrO radical using the UCCSD(T) and MRCI methods with the TZ2P(2SP) and cc-pVTZ basis sets. The optimized values of 1.745 Å at the MRCI/TZ2P(2SP) level and 1.743 Å at the UCCSD(T)/TZ2P(2SP) level, respectively, are both consistent with the previously optimized value (1.746 Å at the UCCSD(T)/TZ2P level by Francisco et al.,\(^{7}\) indicating that the two sets of sp diffuse functions in the TZ2P(2SP) basis set do not have a large effect. However, they are all larger by about 0.025 Å than the experimental value of 1.721 Å (SO averaged value).\(^{2}\) The optimized bond lengths with the cc-pVTZ basis set are 1.735 and 1.732 Å for UCCSD(T) and

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>UCCSD(T)</th>
<th>MRCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrO</td>
<td>TZ2P(2SP)</td>
<td>cc-pVTZ</td>
</tr>
<tr>
<td></td>
<td>1.743</td>
<td>1.735</td>
</tr>
</tbody>
</table>

TABLE I. Optimized geometries (in Å) for the ground state of BrO.
of spin–orbit coupling effects (Å and cm⁻¹). Experimental values are in parentheses.

<table>
<thead>
<tr>
<th>State</th>
<th>Tₑ (eV)</th>
<th>rₑ(BrO)</th>
<th>ωₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>X ¹Σ⁺</td>
<td>0.00</td>
<td>1.729</td>
<td>727</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.7206)</td>
<td>(725)</td>
</tr>
<tr>
<td>X₁ ³Π₁/₂</td>
<td>0.00</td>
<td>1.727</td>
<td>730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.7172)</td>
<td>(733)</td>
</tr>
<tr>
<td>X₂ ³Π₁/₂</td>
<td>0.09</td>
<td>1.733</td>
<td>719</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.12)</td>
<td>(718)</td>
</tr>
<tr>
<td>A ¹Σ⁺</td>
<td>3.41</td>
<td>1.943</td>
<td>532</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.27)</td>
<td>(478)</td>
</tr>
</tbody>
</table>

The vertical excitation energies calculated at the MRCI level of theory with the TZ2P(2SP) and cc-pVTZ basis sets are summarized in Table IV. The vertical excitation energies were calculated with both the multipurpose Davidson and Pople corrections for higher excitations. In Table IV, only the Davidson corrected results (+Q) are included; however, we did find that the Pople corrections agreed well with the Davidson corrections to within 0.01 eV in all cases. Based on the vertical excitation energy values, the ordering of the excited states is 2¹Π, 1³Δ, 1³Σ⁻, and 1¹Σ⁺. To evaluate whether the inclusion of scalar relativistic effects would change the order of these states, the vertical excitation energies were recalculated using relativistic effective core potentials (ECPs). The ECP basis set for bromine was used with the cc-pVTZ basis set for oxygen in the calculations. The results shown in Table IV show that the order of these states is not changed by scalar relativistic effects, nor are the vertical excitation energies significantly affected.

As can be seen in Table III, the main configuration for the 2¹Π state is (Core)9σ²10σ²11σ²1π²2π⁴, which is derived from a 1π→2π electron transition relative to the ground state configuration (Core)9σ²10σ²11σ²1π²2π⁴. The vertical excitation energy for the 2¹Π state is 3.81 eV (i.e., 325 nm) with the TZ2P(2SP) basis set, and 3.94 eV (i.e., 315 nm) with the cc-pVTZ basis set, which is consistent with the experimental finding that the X ²Π→A ¹Π absorption spectrum is in the 280–380 nm region. The difference between our calculated vertical excitation energy (MRCI) for the 2¹Π state and the experimental strongest absorption feature around 338 nm (i.e., 3.67 eV) is 0.14 eV with the TZ2P(2SP) and 0.30 eV with the cc-pVTZ basis set. This suggests that the TZ2P(2SP) basis set is more appropriate than the cc-pVTZ for the vertical excitation energies. This may be due to the fact that the TZ2P(2SP) basis set includes two sets of sp diffuse functions, but the cc-pVTZ basis set does not include any additional diffuse functions.

The 1³Δ and 1³Σ⁻ states have the same main configuration, (Core)9σ²10σ²11σ²1π²2π⁴, which derives from the electron transition 2π→12σ relative to the ground state. The 1³Σ⁻ state corresponds to the electron transition 11σ→2π. As far as we know, there is no experimental vertical excitation energy available for the excited states (1³Σ⁺, 1³Σ⁰, and 1³Σ⁻).
In order to understand the mechanism of predissociation for the $A^2 \Pi$ excited state, the potential energy curves for the ground state and several low-lying excited doublet states were computed at the MRCI+Q/aug-cc-pVQZ level of theory and are shown in Fig. 1.

The MRCI+Q/aug-cc-pVQZ calculations provide the most consistent results about the potential energy curves of the ground state, $1^2 \Pi$, and the four low-lying excited states, $2^2 \Pi, 1^2 \Delta, 1^2 \Sigma^-, and 1^2 \Sigma^-$. The ground state has a minimum around 1.7 Å and dissociates to $\text{O}(^3 \Pi) + \text{Br}(^2 P)$. Compared to the ground state, the first excited state ($2^2 \Pi$) has a minimum at a larger Br–O distance around 2.0 Å, which is consistent with the electronic transition $1 \pi \rightarrow 2 \pi$. As previously discussed, $1 \pi$ is the bonding molecular orbital between the 4p orbital of Br and 2p of the O atom, while the 2\pi is the corresponding antibonding molecular orbital. The electronic transition from $1 \pi$ to $2 \pi$ weakens the Br–O bond and lengths the Br–O distance. The bound $2^2 \Pi$ state diabatically correlates to the dissociation limit that yields the products $\text{Br}(^2 P) + \text{O}(^3 \Pi)$; however, there are a total of five repulsive doublet states, the $1^2 \Delta, 1^2 \Sigma^-, 1^2 \Sigma^+, 2^2 \Sigma^-$, and the $3^2 \Pi$, that intersect the $2^2 \Pi$ state (i.e., the $A^2 \Pi$) at Br–O bond distances between 1.9 and 2.4 Å. Just as in the case of ClO, these intersections result in predissociation to products on the ground state surface, namely Br($^2 P$) + O($^3 P$), and the predissociation characteristic of the $A^2 \Pi$ potential energy curve is the reason for the diffuse vibrational structure of the $X^2 \Pi \rightarrow A^2 \Pi$ absorption spectrum.

While a detailed investigation of the predissociation mechanism of the $A^2 \Pi$ state of BrO is beyond the scope of the present work, calculations are currently being carried out that include both the accurate determination spin–orbit and nonadiabatic derivative coupling matrix elements required for the theoretical calculation of predissociation linewidths.

Spectroscopic constants for the $A^2 \Pi$ state of BrO calculated at the MRCI+Q/aug-cc-pVQZ level of theory are also shown in Table II. The effects of spin–orbit coupling on this state are also relatively strong, with shifts of the equilibrium excitation energy ($T_e$), bond length, and harmonic frequency of $-0.06 \text{ eV}$, $+0.002 \text{ Å}$, and $-54 \text{ cm}^{-1}$ ($A^2 \Pi \rightarrow A^2 \Pi_{1/2}$). Vertical excitation energies calculated at the same level of theory (without SO coupling) are also shown in Table IV and are in good agreement with the previously discussed MRCI calculations. The inclusion of SO effects, while increasing the number of electronic states ($10L\rightarrow S$ states $\rightarrow 15 \Omega$ states), does not qualitatively change the ordering of the electronic states.

Potential energy curves for the quartet states of BrO are shown in Fig. 2. Similar to the case of ClO, all of the quartet states are repulsive except for the low-lying $1^4 \Sigma^-$ state, which is bound and represents the first excited state of BrO with a calculated vertical excitation energy at the MRCI+Q/aug-cc-pVQZ level of theory of $2.88 \text{ eV}$. The other quartet states all have vertical excitation energies above $5.7 \text{ eV}$. The $1^4 \Sigma^-$ state has not been observed experimentally, however while the $X^2 \Pi \rightarrow 1^4 \Sigma^-$ transition is formally spin-forbidden the spin–orbit coupling in BrO may be sufficiently strong to facilitate its observation.

**IV. CONCLUSION**

In this work, using high level ab initio methods (CASSCF and MRCI), we have computed the potential energy curves and vertical excitation energies for many of the excited states of BrO, including the $2^2 \Pi, 1^2 \Delta, 1^2 \Sigma^-, and 1^2 \Sigma^+$. The possible electronic states leading to the predissociation of the $2^2 \Pi$ state has been uncovered. The $2^2 \Pi$...
state is intersected by five repulsive states, the $1^{2}\Delta$, $1^{2}\Sigma^-$, $1^{2}\Sigma^+$, $2^{2}\Sigma^-$, and $3^{2}\Pi$, which results in predissociation to Br(2$P$) + O(3$P$).

**Note added in proof.** A recent experiment study\(^3\) of BrO has estimated the location of the $3^{2}\Sigma^+$ state using a single perturber approximation method. The authors find this state using the method to be located at 3.41 eV which is consistent with results from the vertical excitation energy location of the $2^{2}\Sigma^+$ state given in Table IV.

**ACKNOWLEDGMENT**

K.A.P. was supported by the Division of Chemical Sciences in the Office of Basic Energy Sciences of the U.S. Department of Energy at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle Memorial Institute, under Contract No. DE-AC06-76RLO 1830.

\(^1\) P. O. Wennberg et al., Science 266, 398 (1994).