A theoretical study on the inner-valence photoelectron spectra lying between 21 and 26 eV of the O_2 molecule

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Ab initio calculations were carried out to study the structures of the photoelectron spectra of the O_2 molecule using complete active space self-consistent field and multireference single and double excitation configuration interaction methods. We focused our attention primarily on the inner-valence ionized states lying below 26 eV. Vibrational levels were calculated using adiabatic potential curves and vibrational wave functions were used to obtain Franck–Condon factors. We show that not only discrete vibrational levels of $(3)\,^2\Pi_u$, but also the continuum of nuclear motion in $(1)\,^2\Sigma_u^-$ contribute to the bands of vibrational progression and the broad peak of the continuum between 22.5 and 26 eV. Other states with weak intensity lying between 19 and 26 eV are also discussed. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1834565]

I. INTRODUCTION

The O_2 molecule has been studied by many authors using photoelectron spectroscopy with He(I) or He(II) and threshold photoelectron spectroscopy with synchrotron radiation.[1–5] The vibrational structures of the lower five electronic states lying between 12 and 21 eV are very well resolved. Assignment of these levels are established to be the $X\,^2\Pi_g$, $a\,^4\Pi_u$, $A\,^2\Pi_u$, $b\,^4\Sigma_g^-$, and $B\,^2\Sigma_g^-$ states from the side with lower energy.

The two strong peaks found around 24.8 eV were analyzed theoretically by Tanaka and Yoshimine[6] and they assigned these two peaks to the $c\,^4\Sigma_u^-$ state. The state was classified as the ionization of $2s\,\sigma_u$ (inner-valence ionization). Other than these peaks, a few vibrational bands and a continuum lying between 22.5 and 26 eV have been reported by Baltzer and co-workers[4] using a high-resolution uv (ultra violet) photoelectron spectra. They assigned the vibrational levels to the third $^2\Pi_u$ state, $(3)\,^2\Pi_u$. The origin of the continuum beyond 23.6 eV with a very broad peak around 23.8–23.9 eV has not yet been clarified. Furthermore Ellis and co-workers[5] reported the threshold photoelectron spectra between 20 and 26 eV. They found new weak vibrational progressions between 21 and 22.4 eV, which were not observed by photoelectron spectroscopy. These bands were thought to have originated from autoionizing Rydberg states of O_2, which converges to $(3)\,^2\Pi_u$, because the shape of the vibrational progressions were similar to that of the $(3)\,^2\Pi_u$ state. They also proposed a possible mechanism of autoionization in this case. Morioka and co-workers[7] discussed the possibility of assigning these new weak vibrational levels to the $^4\Pi_u$ and $^4\Pi_g$ states, based on a theoretical study by Beebe and co-workers.[8] Furthermore, the inner-valence region was analyzed in more detail by Tanaka and co-workers.[9] They discussed the threshold photoelectron spectra in the 18–24 eV region including very weak $(1)\,^2\Phi_u$, $(2)\,^2\Pi_u$, $(1)\,^2\Delta_g$, $(1)\,^2\Sigma_u^-$, $(1)\,^4\Pi_g$, and $(2)\,^4\Pi_u$ states.

Rolke and co-workers[10] carried out extensive experimental and theoretical analyses using electron momentum spectroscopy including the inner-valence region. A theoretical study of the photoelectron spectra of O_2 at levels higher than 26 eV was reported by Hikosaka and co-workers.[11] In the present study, we focused our attention primarily on the photoelectron spectra and the threshold photoelectron spectra observed between 19 and 26 eV, and we discuss here the assignment and characteristics of these levels. We calculated the potential energy curves of O_2^+ and vibrational energy levels which are below 26 eV relative to the ground state of O_2 (briefly refereed to as "ground state" hereafter). The vibrational wave functions were obtained using the potential curves. Franck–Condon factors between the ground state and the O_2^+ states were calculated in order to analyze the spectra.

Many wave functions of these higher energy states are not represented by a single configuration, but are represented essentially by multiconfigurations. In this study, we employed a configuration interaction method to describe the electronic wave functions.

II. METHOD OF CALCULATIONS

We used the MIDI-4 basis set prepared by Tatewaki and Huzinaga.[12] This set was augmented by one primitive *d*-type polarization function whose exponent is 1.16.

A complete active space self-consistent-field (CASSCF) method was employed, in which the $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals were selected to compose an active orbital space and 11 valence electrons were distributed among the orbitals. We selected reference configuration state functions (CSFs) whose coefficients were larger than 0.01 in the CASSCF calculations. Using the CSFs as reference func-

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tions and the molecular orbitals obtained by the CASSCF calculations, we obtained the potential energy curves by multireference single and double excitation configuration interaction (MRSDCI) calculations. The number of CSFs ranged from 104 889 to 157 536. CASSCF and MRSDCI calculations were carried out using the program codes of ALCHEMYII.[13–15]

We calculated the vibrational energy levels and the wave functions using the discrete variable representation method (DVR).[16] The Franck–Condon factors (FCFs) between the ground state and the cationic states were calculated. Theoretical intensity lines were obtained using the FCFs and the weight of the CSF, which was generated by one electron ionization from the leading CSF of the ground state:

$$\cdots 3\sigma_g^2 1\pi_u^4 \{1\pi_g^2\}^{3}\Sigma_g^- . \quad (1)$$

For example, the electronic transition intensities of the $X\,^2\Pi_g$, $a\,^4\Pi_u$, $A\,^2\Pi_u$, $b\,^4\Sigma_g^-$, and $B\,^2\Sigma_g^-$ states were estimated by the weights of the following CSFs:

$$\cdots 3\sigma_g^2 1\pi_u^4 1\pi_g^1 \quad \text{for } {}^2\Pi_g \text{ state}, \quad (2)$$

$$\cdots 3\sigma_g^2 1\pi_u^3 \{1\pi_g^2\}^{3}\Sigma_g^- \quad \text{for } {}^{4,2}\Pi_u \text{ states}, \quad (3)$$

$$\cdots 3\sigma_g^1 1\pi_u^4 \{1\pi_g^2\}^{3}\Sigma_g^- \quad \text{for } {}^{4,2}\Sigma_g^- \text{ states}. \quad (4)$$

III. RESULTS AND DISCUSSION

A. Energy range between 12 and 21 eV

Before proceeding to a discussion of the energy range of 21–26 eV, we will discuss the present calculated spectra ranging between 12 and 21 eV, and we will compre the calculated spectra with the observed spectra. The purpose is to demonstrate how our computational scheme is appropriate for study of the photoelectron spectra. In this energy region, five electronic states contribute to the vibrational progressions of the photoelectron spectra, namely, the $X\,^2\Pi_g$, $a\,^4\Pi_u$, $A\,^2\Pi_u$, $b\,^4\Sigma_g^-$, and $B\,^2\Sigma_g^-$ states. Figure 1 shows the potential energy curves of seven electronic states which appear in the energy range of 12–21 eV. They have energy minima near the observed equilibrium internuclear distance of the ground state [1.207 Å (Ref. 17)]. Table I shows the calculated bond distances and the 0-0 ionization energies of

TABLE I. Bond distance R_e, 0-0 ionization energy $E_{(0\text{-}0)}$, and type of ionization of the lowest five electronic states.

	Re (Å)		$E_{(0\text{-}0)}$ (eV)		Type of ionization	
State	Obs[a]	Calc	Obs[b]	Calc	Main configuration	Weight[c]
$X\,^2\Pi_g$	1.12	1.13	12.07	11.61	$1\pi_g \rightarrow \infty$	0.85
$a\,^4\Pi_u$	1.38	1.43	16.10	15.41	$1\pi_u \rightarrow \infty$	0.91
$A\,^2\Pi_u$	1.41	1.45	17.05	16.43	$1\pi_u \rightarrow \infty$	0.33
$b\,^4\Sigma_g^-$	1.28	1.29	18.17	17.57	$3\sigma_g \rightarrow \infty$	0.88
$B\,^2\Sigma_g^-$	1.29	1.30	20.30	19.86	$3\sigma_g \rightarrow \infty$	0.65

[a]Reference 17.
[b]Reference 2.
[c]Weight of the CSFs specified by Eqs. (2), (3), and (4).

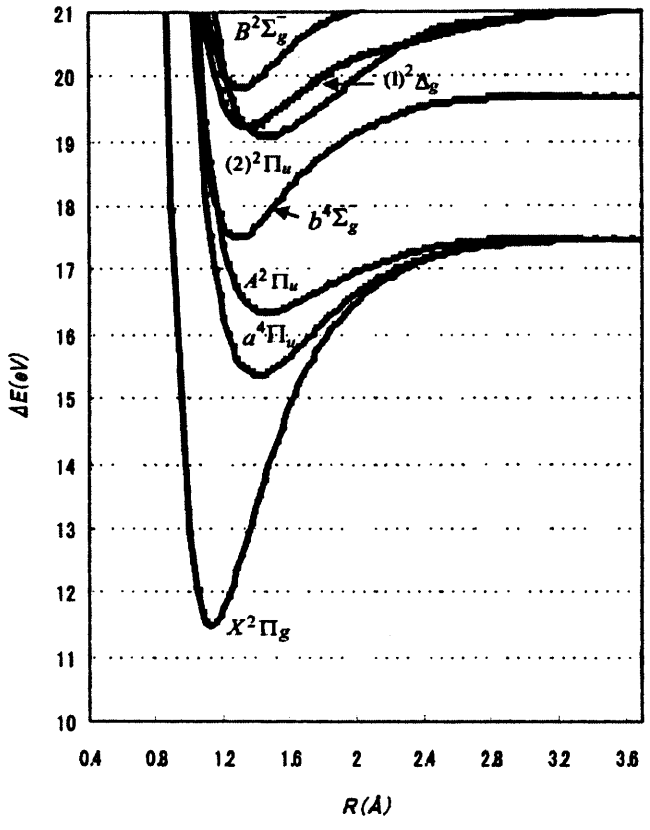

FIG. 1. Adiabatic potential energy curves of the lower seven states of O_2^+.

$X\,^2\Pi_g$, $a\,^4\Pi_u$, $A\,^2\Pi_u$, $b\,^4\Sigma_g^-$, and $B\,^2\Sigma_g^-$; the calculated results are compared with the observed ones.

The calculated bond distances were found to agree well with the observed distances within 0.05 Å. The calculated bond length of the ground state was 1.216 Å, which is in good agreement with the observed value. The 0-0 ionization energies were underestimated by 0.44–0.69 eV. As was discussed in the preceding section, the CSFs of Eqs. (2), (3), and (4) are essentially one electron ionization from the ground state CSF, Eq. (1). The intensity of each vibrational level was estimated as a product of the weight of the CSFs given in Table I and the FCF. The weights were obtained at the equilibrium distance of the ground state. The weights of the $A\,^2\Pi_u$ and $B\,^2\Sigma_g^-$ states were rather small. The remaining weights of $A\,^2\Pi_u$ were distributed to primarily among the CSFs of the same configuration but with different spin coupling and those of $B\,^2\Sigma_g^-$ are distributed to different configurations.

Figure 2 shows the theoretical intensity lines for the five states, and these spectra are compared with the observed photoelectron spectra observed by Kimura and co-workers.[3] Judging from the good agreement between the vibrational-level spacing and intensity with the observed results, the present approach appears to be well designed for describing the potential curves and wave functions.

Even though the potential curves of these states appeared in the energy range given in Fig. 1, no peaks of the $^2\Delta_g$ and $(2)\,^2\Pi_u$ states were observed, because (1) the leading CSF of the $^2\Delta_g$ state

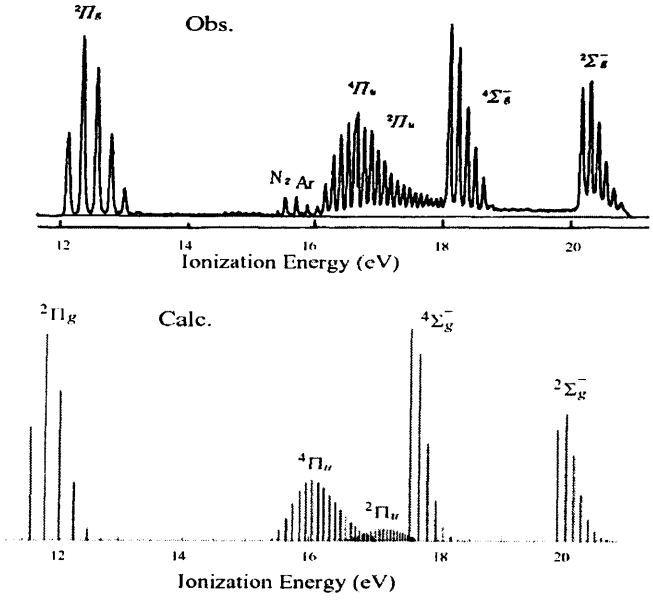

FIG. 2. Comparison of the intensity lines of the lower five electronic states; obs, upper panel (taken from Ref. 3), and present calc, lower panel.

$$\cdots 3\sigma_g^1 1\pi_u^4\{1\pi_g^2\}^1\Delta_g, \tag{5}$$

indicates that the transition intensity from the ground state is very small, because of the different spatial and spin coupling in the $1\pi_g^2$ shell function; and (2) the leading CSF of the $(2)\,^2\Pi_u$ state is

$$\cdots 3\sigma_g^2 1\pi_u^3\{1\pi_g^2\}^1\Delta_g. \tag{6}$$

Thus, the transition intensity is very small for the same reason. Only slightly below the $(2)\,^2\Pi_u$ state, there exists the $(1)\,^2\Phi_u$ state, which is represented by $\cdots 3\sigma_g^2 1\pi_u^3\{1\pi_g^2\}^1\Delta_g$. The $1\pi_g$ shell function of the leading CSF of the state is also $\{1\pi_g^2\}^1\Delta_g$, as in the case of $(2)\,^2\Pi_u$. We will discuss these states in Sec. III C.

B. Energy range between 21 and 26 eV

The photoelectron spectra between 21 and 26 eV exhibit the following three features. Resolved vibrational levels were observed in the range of 22.3–23.7 eV, which was previously assigned to the $(3)\,^2\Pi_u$ state by Baltzer and co-workers.[4] A continuum followed above 23.7 eV; the origin of this continuum has not yet been clarified. Two strong peaks appeared at 24.6 and 24.8 eV, which have been established as the quasibound vibrational levels of the $c\,^4\Sigma_u^-$ state.[6] This scheme is illustrated in Fig. 3, which includes the photoelectron spectra observed by Baltzer and co-workers.[4]

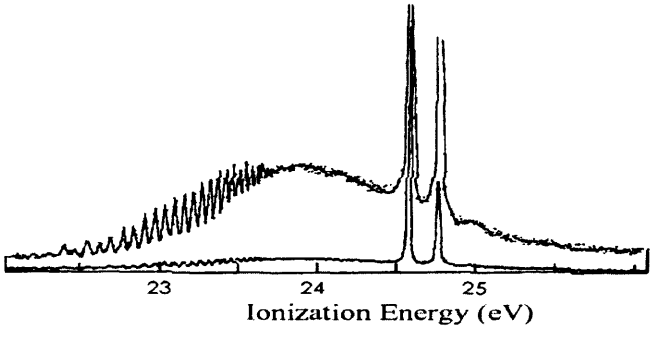

FIG. 3. Observed photoelectron spectra ranging between 22 and 26 eV, taken from Baltzer *et al.* (Ref. 5).

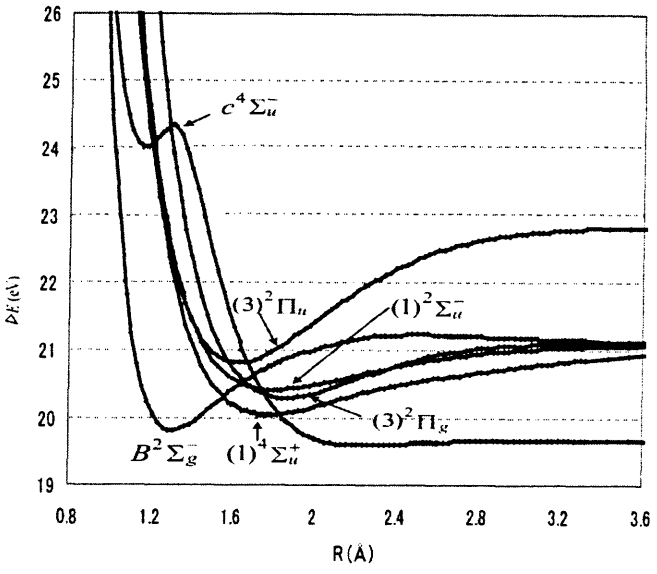

FIG. 4. Potential curves of the inner-valence ionized states.

Figure 4 shows six potential energy curves lying between 19 and 26 eV, where each curve has a minimum (or a local energy minimum) at a bond length of less than 2 Å. These states provide non-negligible FCF values. The $B\,^2\Sigma_g^-$ is the highest state discussed in the preceding section. The $c\,^4\Sigma_u^-$ state has a shallow potential well near 1.2 Å, and the well is the origin of the two quasibound vibrational levels. The state is represented by a CSF,

$$\cdots 2\sigma_u^1 3\sigma_g^2 1\pi_u^4\{1\pi_g^2\}^3\Sigma_g^-. \tag{7}$$

A detailed discussion of the state is given by Tanaka and Yoshimine.[6]

Among the remaining four states, $(1)\,^4\Sigma_u^+$, $(3)\,^2\Pi_g$, $(3)\,^2\Pi_u$, and $(1)\,^2\Sigma_u^-$, the wave functions of the $(3)\,^2\Pi_u$ and $(1)\,^2\Sigma_u^-$ states include the CSFs of Eqs. (3) and (7), respectively, with considerable weight, whereas the primary electronic configurations of the $(1)\,^4\Sigma_u^+$ and $(3)\,^2\Pi_g$ states are not the ones represented by an electron ionization from the ground state CSF. The intensity of the latter two states is negligibly small in this energy range.

Table II gives the calculated bond distances and the 0-0

TABLE II. Bond distance R_e, 0-0 ionization energy $E_{(0\text{-}0)}$, and type of ionization of the $(3)\,^2\Pi_u$, $(1)\,^2\Sigma_u^-$, and $c\,^4\Sigma_u^-$ states.

State	Re (Å) Calc	$E_{(0\text{-}0)}$ (eV) Calc	Type of ionization	
			Main configuration	Weight[a]
$(1)\,^2\Sigma_u^-$	1.80	20.44	$2\sigma_u \rightarrow \infty$	0.31
$(3)\,^2\Pi_u$	1.62	20.90	$1\pi_u \rightarrow \infty$	0.46
$c\,^4\Sigma_u^-$	1.16	24.03	$2\sigma_u \rightarrow \infty$	0.85

[a]Weight of the CSFs specified by the CSF (3) for $^2\Pi_u$ and CSF (7) for $^{4,2}\Sigma_u^-$ in the text.

TABLE III. Vibrational levels of the (3) $^2\Pi_u$ state.

	Present			Baltzer *et al.* (calc)[a]			(Obs)[a]	
Level	Energy	ΔE[b]	FCF[c]	Energy	ΔE[b]	FCF[c]	Energy	ΔE[b]
0	20.901	···	d	21.490	···	d		
1	20.995	0.094	d	21.584	0.094	d		
2	21.087	0.092	d	21.682	0.098	d		
3	21.177	0.090	d	21.784	0.102	d		
4	21.266	0.089	d	21.882	0.098	d		
5	21.354	0.088	1	21.977	0.095	1		
6	21.441	0.087	2	22.068	0.091	3		
7	21.525	0.085	5	22.156	0.088	6		
8	21.607	0.082	11	22.242	0.086	13		
9	21.687	0.080	20	22.326	0.084	24	22.300	
10	21.765	0.077	36	22.409	0.083	43	22.393	0.093
11	21.840	0.075	60	22.490	0.081	72	22.461	0.068
12	21.914	0.074	94	22.570	0.080	113	22.538	0.077
13	21.986	0.072	142	22.648	0.078	168	22.616	0.078
14	22.056	0.070	203	22.723	0.075	240	22.684	0.068
15	22.125	0.069	280	22.797	0.074	328	22.763	0.079
16	22.192	0.067	370	22.869	0.072	432	22.833	0.070
17	22.257	0.065	473	22.939	0.070	549	22.900	0.067
18	22.319	0.063	585	23.007	0.068	678	22.965	0.065
19	22.380	0.060	703	23.072	0.065	815	23.029	0.064
20	22.438	0.058	823	23.135	0.063	955	23.091	0.062
21	22.494	0.056	942	23.196	0.061	1090	23.148	0.057
22	22.548	0.054	1055	23.254	0.058	1230	23.205	0.057
23	22.599	0.051	1159	23.310	0.056	1340	23.257	0.052
24	22.648	0.049	1249	23.364	0.054	1440	23.309	0.052
25	22.695	0.047	1320	23.414	0.050	1510	23.361	0.052
26	22.739	0.044	1366	23.462	0.048	1520	23.408	0.047
27	22.781	0.042	1383	23.506	0.044	1430	23.452	0.044
28	22.820	0.039	1368	23.546	0.040	1220	23.494	0.042
29	22.855	0.035	1319	23.581	0.035	909	23.534	0.040
30	22.887	0.032	1239				23.572	0.038
31	22.915	0.028	1130				23.602	0.030
32	22.939	0.024	993				23.638	0.036
33	22.959	0.020	822				23.664	0.026
34	22.975	0.016	607				23.689	0.025
35	22.985	0.010	339				23.708	0.019
36							23.732	0.024

[a]Reference 4.
[b]Vibrational energy level spacing.
[c]Given in unit of 10^{-5}.
[d]Less than 10^{-5}.

ionization energies of (1) $^2\Sigma_u^-$, (3) $^2\Pi_u$, and $c\,^4\Sigma_u^-$. Since the (3) $^2\Pi_u$ state has a deep potential well, we obtained discrete vibrational levels which have non-negligible FCFs in the range between 21.8 and 22.9 eV. A continuum follows above 22.9 eV, which corresponds to the energy of the dissociation limit. Table III gives the discrete vibrational energy levels and the FCFs, which are compared with the calculated and observed values by Baltzer and co-workers.[4] The maximum intensity obtained by the present calculations was located at 22.78 eV of the 27th level and was underestimated by ca. 0.7 eV when compared to the observed value. The present level spacing and FCFs are in good agreement with Baltzer's calculated results.

The (1) $^2\Sigma_u^-$ state contains 24 discrete vibrational levels below 21.1 eV, but the FCFs are much smaller than the discrete levels of (3) $^2\Pi_u$. A continuum higher than 21.1 eV follows with non-negligible intensity for (1) $^2\Sigma_u^-$. As was described in the preceding section, we estimated the ionization intensity of (3) $^2\Pi_u$ and (1) $^2\Sigma_u^-$ using the FCFs and the weight of the leading one electron ionization CSFs of Eqs. (3) and (7) (see Table II). The theoretical intensity lines of these two states, multiplied by 50, are illustrated in Fig. 5, in which the intensity lines of the $c\,^4\Sigma_u^-$ state are also included for comparison. The discrete vibrational levels of the (1) $^2\Sigma_u^-$ state are not included in the figure due to the negligibly low intensity.

Figure 6 illustrates the addition of the intensity line of the (3) $^2\Pi_u$ and (1) $^2\Sigma_u^-$ states for two intensity ratios between the two states. If we compare the shape of the observed progression (Fig. 3) with the calculated progression, the shape of the case involving the 1:3 ratio of the calculated progression is in good agreement with the observed progression except for the portion that is strongly dependent on the curvature of the adiabatic potential curve of (3) $^2\Pi_u$ near the dissociation limit. The present results indicate that the ob-

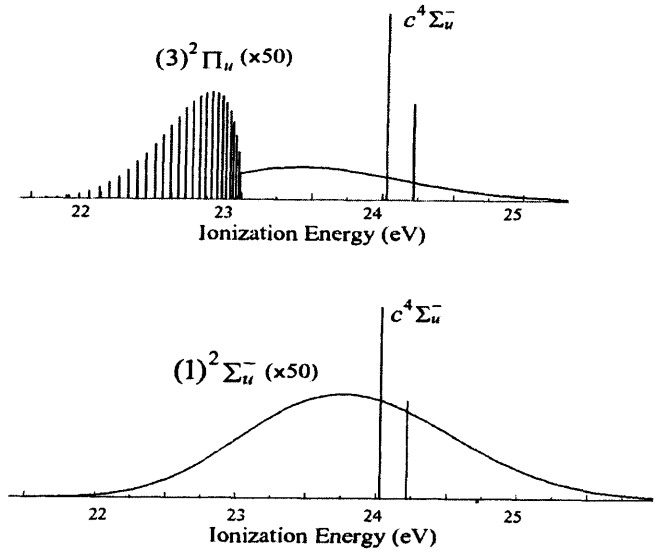

FIG. 5. Intensity of $(3)\,^2\Pi_u$ and $(1)\,^2\Sigma_u^-$ (the intensity lines of $c\,^4\Sigma_u^-$ are included for comparison).

served intensity bands from 22.3 to 23.7 eV are composed of discrete vibrational levels of $(3)\,^2\Pi_u$ and the continuum intensity from $(1)\,^2\Sigma_u^-$. The continuum from 23.7 to 26 eV are derived primarily from $(1)\,^2\Sigma_u^-$. Since the weight of CSF (7) is 0.31 in $(1)\,^2\Sigma_u^-$, the higher $^2\Sigma_u^-$ states are expected to contribute to the photoelectron spectra.

Ellis and co-workers[5] recorded the threshold photoelectron spectra between 20 and 26 eV. Two progressions of weak vibrational levels were found between 21 and 22.4 eV, and these levels were not observed upon photoelectron spectroscopy. There were no ionization states that provided the same order of intensity as those of $(3)\,^2\Pi_u$ in this energy region. We expect that the spectra were not result of direct ionization.

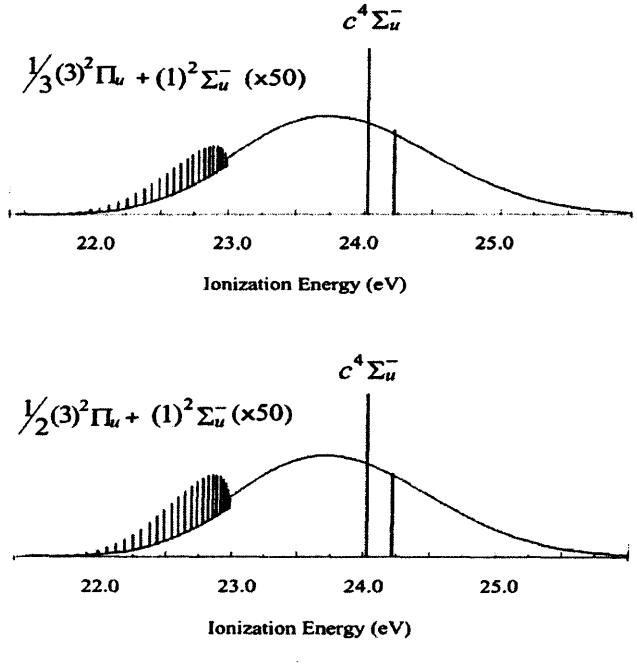

FIG. 6. Addition of the intensities of $(3)\,^2\Pi_u$ and $(1)\,^2\Sigma_u^-$.

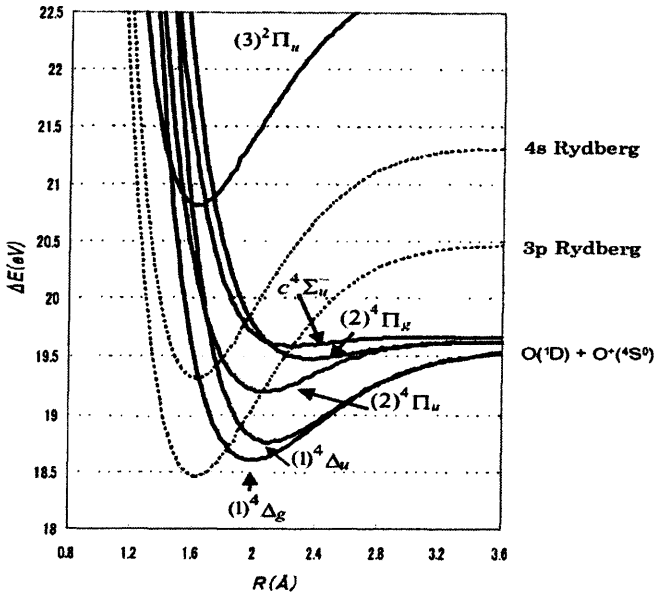

FIG. 7. Estimated potential curves of Rydberg states, as well as the calculated potential curves of $(3)\,^2\Pi_u$ and some quartet states dissociating to $O(^1D)+O^+(^4S^\circ)$.

Ellis and co-workers suggested that the progressions are caused by autoionization from Rydberg states converging to the $(3)\,^2\Pi_u$ state. Resemblance of the vibrational spectra of both progressions to those of $(3)\,^2\Pi_u$ appears to support this line of reasoning. Possible candidates of the Rydberg states are as follows:

$$[\{\cdots 3\sigma_g^2 1\pi_u^3 1\pi_g^2\}^{2}\Pi_u 3p^1]^{3}\Pi_u,{}^{3}\Sigma_u^-,$$

$$[\{\cdots 3\sigma_g^2 1\pi_u^3 1\pi_g^2\}^{2}\Pi_u 4s^1]\ {}^{3}\Pi_u.$$

If we draw the $3p$ (Ref. 18) and $4s$ Rydberg-type potential curves using the potential curve of $(3)\,^2\Pi_u$ with a quantum defect of 0.6 for $3p$ and 1.0 for $4s$, the curves of the Rydberg states lie below the $(3)\,^2\Pi_u$ state by 2.36 and 1.51 eV. Recalling that the theoretical maximum intensity of $(3)\,^2\Pi_u$ is located at 22.78 eV, the positions of the maximum intensity of the Rydberg states are estimated to be 20.4 and 21.3 eV for the $3p$ and $4s$ type states, respectively. If we add the underestimation of 0.7 eV for the ionization energy of the $(3)\,^2\Pi_u$ state to these energies, the energetical position of the maximum peaks of the Rydberg states are estimated to be 21.1 and 21.9 eV, a finding which is in good agreement with the observed maximum peaks of 21.2 and 21.8 eV.

Figure 7 shows the estimated Rydberg potential curves as dotted lines; the calculated potential curves of $(3)\,^2\Pi_u$, $c\,^4\Sigma_u^-$, $(1)\,^4\Delta_g$, $(1)\,^4\Delta_u$, $(2)\,^4\Pi_u$, and $(2)\,^4\Pi_g$ are also shown. It should be noted that the potential curves of the Rydberg states cross the potential curves of these quartet states, which dissociated to $O(^1D)+O^+(^4S^\circ)$. The calculated dissociation limit is 19.7 eV by the present calculations (versus 20.7 eV by observation). Since onset of the progression of the threshold photoelectron spectroscopy is 21 eV and O^+ is observed by coincidence, it becomes apparent that autoionization to these quartet states takes place through

TABLE IV. Term energy, vibrational frequency, and bond distance of the states ranging between 19 and 22 eV with weak intensity.

State	T_e (eV)		ω_e (cm^{-1})		Re (Å)
	Obs	Calc	Obs	Calc	Calc
(1) $^2\Phi_u$	18.69	17.98	1017	946	1.41
(2) $^2\Pi_u$	19.58	19.07	876	743	1.46
(1) $^2\Delta_g$	19.72	19.81	1007	1070	1.30
(1) $^2\Sigma_u^-$	20.30	20.42	826	423	1.80
(1) $^4\Pi_g$	21.09	20.58	582	305	2.30
(2) $^4\Pi_u$	21.39	20.83	541	224	2.71
(1) $^4\Sigma_u^+$	···	20.05	···	476	1.77

nonadiabatic coupling after excitation to the Rydberg states. We therefore are in agreement with the conclusion of Ellis and co-workers.[5]

C. Very weak discrete vibrational levels

Tanaka and co-workers[9] found a new very weak vibrational level at ca. 19.58 eV. They proposed the (2) $^2\Pi_u$ state as an attractive candidate for this newly observed state. Other than this state, they discussed (1) $^2\Phi_u$, (1) $^2\Delta_g$, and (1) $^2\Sigma_u^-$, which were also observed and identified.[4,19] In Table IV, we compare the calculated T_e and ω_e values of these states with those summarized by Tanaka and co-workers.[9] The calculated R_e's of these states are also included in Table IV.

Among the four doublet states included in Table IV, the present T_e and ω_e values of the identified states, (1) $^2\Phi_u$, (1) $^2\Delta_g$, and (1) $^2\Sigma_u^-$, agree well with the experimental values. Judging from the same level of agreement with the experimental values for the newly observed state, the present results support the assignment of (2) $^2\Pi_u$ for this state.

Furthermore, Tanaka and co-workers[9] found very weak vibrational levels of two quartet states between the $B\,^2\Sigma_g^-$ and (3) $^2\Pi_u$ states. In the present calculations, only three quartet states exhibited bound potential curves between 20 and 22 eV, i.e., the (1) $^4\Pi_g$, (2) $^4\Pi_u$, and (1) $^4\Sigma_u^+$ states. Since the leading configurations of these states do not include the π_g shell function of $\{\pi_g^2\}^3\Sigma_g^-$, the probability of electronic transition to these states is expected to be very small. Taking into account Beebe's results,[8] Tanaka and coworkers identified two observed states, the T_e values of which are 21.09 and 21.39 eV, as $^4\Pi_g$ and $^4\Pi_u$, respectively. The present results support these assignments, which should be (1) $^4\Pi_g$ and (2) $^4\Pi_u$. The (1) $^4\Sigma_u^+$ state is slightly lower in energy than these two states. Since the R_e value of the (1) $^4\Sigma_u^+$ state is very close to that of the ground state in comparison with those of the other two quartet states, FCFs of the (1) $^4\Sigma_u^+$ state should be larger than the other two quartet states. The reason why (1) $^4\Sigma_u^+$ has not been observed might be that the energy range of this state overlaps with that of the vibrational levels of $B\,^2\Sigma_g^-$.

IV. CONCLUDING REMARKS

We studied the potential energy curves of the O_2^+ molecule below 26 eV relative to the ground state using CASSCF and MRSDCI methods with a DZ+P basis set. We calculated the vibrational levels of O_2^+, including the continuum levels, and obtained the theoretical intensity lines. In estimating the intensities, we used not only Franck–Condon factors but also the CSF weights generated by one electron ionization from the ground state CSF as follows:

$$\cdots 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 \{1\pi_g^2\}^3\Sigma_g^-.$$

The vibrational structure of the theoretical intensity lines below 21 eV reproduces the photoelectron spectra very well.

The vibrational progression beginning at about 22.3 eV and broad continuum up to 26 eV is composed of transitions to the third $^2\Pi_u$ and first $^2\Sigma_u^-$ states: the third $^2\Pi_u$ state contributes primarily to the discrete vibrational structure and the first $^2\Sigma_u^-$ state gives broad continuum.

The vibrational structure of the threshold photoelectron spectrum in this region is thought to be caused by autoionization from the $3p$ and $4s$ Rydberg states. We also agree with the assignment of the (2) $^2\Pi_u$ state and (1) $^4\Pi_g$ and (2) $^4\Pi_u$ proposed in a previous study by Tanaka and co-workers.[9]

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