J. Phys. Chem. A **2004,** *108,* 6901−6907

C, D, and E Electronic States of the SO_2^+ Ion Studied Using Multiconfiguration Second-Order Perturbation Theory

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Received: April 4, 2004; In Final Form: June 1, 2004

For exploring the C, D, and E states of the SO_2^+ ion, eight excited states of SO_2^+, 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, 1^2B_1, 2^2B_1, 3^2B_1, and 2^2A_2, have been studied using the complete active-space self-consistent field (CASSCF) and multiconfiguration second-order perturbation theory (CASPT2) methods in conjunction with two contracted atomic natural orbital basis sets, S[6s4p3d1f]/O[5s3p2d1f] (ANO-L) and S[4s3p2d]/O[3s2p1d] (ANO-S) (the 1^2A_1, 1^2B_2, and 1^2A_2 states were previously studied and assigned to the X, A, and B states, respectively). Equilibrium geometries and the v_1 and v_2 vibrational frequencies for the eight excited states were predicted at the CASSCF/ANO-L level. For the eight states, the CASPT2/ANO-L adiabatic excitation energy (T_0) and vertical excitation energy (T_v) values were calculated using the CASSCF/ANO-L geometries, and the CASPT2/ANO-L relative energy (T_v') values to X^2A_1 were calculated at the SO_2 molecular geometry. The CASPT2/ANO-L T_0 ordering is: 1^2B_1, 2^2B_1, 2^2A_2, 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, and 3^2B_1 (in increasing order of energy), and five of these states have shake-up ionization character. We assign the observed C, D, and E states of SO_2^+ to 1^2B_1, 2^2A_1, and 2^2B_2, respectively, and the three calculated states have primary ionization character at the molecular geometry. The CASPT2/ANO-L T_0 values and the CASSCF/ANO-L v_1 and v_2 values for 1^2B_1 and 2^2A_1 are in good agreement with the experimental T_0, v_1, and v_2 values for the C and D states, respectively. The CASPT2/ANO-L T_0 value and the CASSCF/ANO-L v_1 and v_2 values for 2^2B_2 are in reasonable agreement with the experimental T_0, v_1, and v_2 values for the E state, respectively. For preliminarily exploring the potential energy surfaces (PESs), potential energy curves (PECs) of the eight excited states, as functions of the OSO bond angle, were calculated at the CASPT2/ANO-S level, and then in the CASSCF/ANO-L PESs of 1^2B_1 and 2^2A_1 we found other minimum energy geometries which have lower CASPT2/ANO-L energies than the "equilibrium geometries" of the respective states. However, these geometries are far away from the Franck−Condon regions for the ground-state molecule and ion. For preliminarily exploring dissociation processes of SO_2^+, a Jacobi coordinate system (C_s symmetry) was adopted and dissociation potential energy curves (DPECs) for the 1-6$^2A'$ and 1-5$^2A''$ states were calculated at the CASPT2/ANO-S level. The calculations indicate that the $1^2A'$, $2^2A'$, $3^2A'$, $1^2A''$, $2^2A''$, and $3^2A''$ DPECs converge to the first dissociation limit [SO^+ ($X^2\Pi$) + O (^3P_g)]. By considering the correlation relations of the C_s states with the C_{2v} states and our assignments for the C, D, and E states, we conclude that, among the C, D, and E states, only two directly correlate to the first dissociation limit.

Introduction

The sulfur dioxide ion (SO_2^+) plays an important role in atmospheric chemistry.[1] Numerous experimental studies have been devoted to the SO_2^+ ion, including photoelectron spectroscopy,[2,3] electron impact ionization,[4] photoionization,[5,6] photodissociation spectroscopy,[7] and photofragment excitation spectroscopy.[8] Three bands were observed in the photoelectron spectra (see ref 2 and references therein). The X state of SO_2^+ is in the first band and the A and B states are in the second band. In a recent work[9] of ours we have suggested assignments of the X, A, and B states to the 1^2A_1, 1^2B_2, and 1^2A_2 states, respectively, based on our calculations using multiconfiguration second-order perturbation theory and contracted atomic natural orbital basis sets. The third band in the spectra is at least 2.5 eV higher in energy than the second band,[2] and the C, D, and E states of SO_2^+ were observed in the third band. In the present theoretical work we explore the C, D, and E states of the SO_2^+ ion.

The experimental adiabatic ionization potential (AIP) values for the X, C, D, and E states of SO_2^+ were reported to be 12.35, 15.90, 16.34, and 16.51 eV by Wang et al.,[2] and similar values were reported by Holland et al.[3] The adiabatic excitation energy (T_0) values for the SO_2^+ ion are considered to be equal to the differences between the AIP values for excited states and the AIP value for the ground state, and therefore the (experimental) T_0 values for the C, D, and E states of SO_2^+ are 3.55, 3.99, and 4.16 eV, respectively, evaluated using the AIP values of Wang et al.[2] Experimental geometric parameters for the C, D, and E states are not available. Several groups reported their observed vibrational frequencies for the v_1 and v_2 modes in the C, D, and E states (they did not report frequency values for the v_3 mode). For the C state, the experimental v_1 and v_2 values were observed to be 767 and 409 cm^{-1} by Thomas et al.[7] and 806 and 381 cm^{-1} by Holland et al.,[3] respectively. For the D state, the experimental v_1 and v_2 values were observed to be 955 and 411 cm^{-1}, respectively, by Thomas et al.,[7] and recently, a smaller v_2 value of 240 cm^{-1} was reported by Zhang et al.[8] For

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10.1021/jp048524z CCC: $27.50

TABLE 1: Previous Assignments for the C, D, and E States of the SO_2^+ Ion[a]

	C	D	E
Hillier et al. (ref 10, RHF)	$^2B_1$	$^2A_1$	$^2B_2$
Wang et al. (ref 2, exptl)	$^2B_2$	$^2A_1$	$^2B_1$
Holland et al. (ref 3, exptl)	$^2B_2$	$^2A_1$	$^2B_1$
Dujardin and Leach. (ref 5, exptl)	$^2B_2$	$^2A_1$	$^2B_1$
Thomaset al. (ref 7, exptl)	$^2B_1$	$^2B_2$	
Zhang et al. (ref 8, exptl)	$^2A_1$	$^2B_1$	$^2B_2$

[a] Molecular orbitals (in increasing order of energy) for the ground-state SO_2 molecule obtained in the HF/6-31+G(d) calculations: $...(5a_1)^2 (3b_2)^2 (6a_1)^2 (4b_2)^2 (7a_1)^2 (2b_1)^2 (5b_2)^2 (1a_2)^2 (8a_1)^2 (3b_1)^0 (9a_1)^0 (10a_1)^0 ....$

the E state, the experimental v_1 and v_2 values were observed to be 960 and 444 cm^{-1}, respectively, by Holland et al.[3]

Different assignments for the C, D, and E states of the SO_2^+ ion were suggested by different groups, and in Table 1 are listed the previous assignments suggested by six research groups.[2,3,5,7,8,10] In most of the experimental papers,[2,3,5] the C, D, and E states were assigned to the $(2)^2B_2$, $(2)^2A_1$, and $(1)^2B_1$ states (C^2B_2, D^2A_1, and E^2B_1), respectively. Hillier and Saunders[10] suggested the C^2B_1, D^2A_1, and E^2B_2 assignments on the basis of their restricted Hartree−Fock (RHF) calculations. Thomas et al.[7] questioned the assignment of D^2A_1 and proposed the assignments of C^2B_1 and D^2B_2. Zhang et al.[8] suggested an assignment of D^2B_1 and possible assignments of C^2A_1 and E^2B_2, based on their photofragment excitation spectrum experiments. In the present theoretical work, we will try to assign the C, D, and E states of the SO_2^+ ion on the basis of calculations using multiconfiguration second-order perturbation theory.

Dynamic studies[2−6,11] indicate that the C, D, and E states of the SO_2^+ ion could predissociate to the first product limit, SO^+ $(X^2\Pi)$ + O (^3P_g). However, the predissociation mechanisms are not clear. Dujardin and Leach[5] suggested couplings of the C^2B_2 and E^2B_1 states (see the assignments presented in refs 2, 3, and 5) to repulsive $^2B_2$ and $^2B_1$ states, respectively, in the predissociation processes, and Zhang et al.[8] suggested coupling of the D^2B_1 state (see the assignment presented in ref 8) to a repulsive $^2A_2$ state in the predissociation process. The suggestions of these experimental groups imply that there may exist more states in the energy region of the third band. In the present theoretical work, we will preliminarily explore the dissociation mechanisms.

It is known that the CASSCF (complete active space self-consistent field)[13] and CASPT2 (multiconfiguration second-order perturbation theory)[14,15] methods are effective for theoretical studies of excited electronic states of molecules. We have studied 11 electronic states of the SO_2^+ ion by using the CASSCF and CASPT2 methods. In a previous paper,[9] we reported our calculation results on the three lowest lying states of the SO_2^+ ion, 1^2A_1, 1^2B_2, and 1^2A_2, and the results indicate that the three states correspond to the X state in the first band and the A and B states in the second band, respectively. In the present paper, we report the results for the eight higher lying electronic states, including the predicted equilibrium geometries, vibrational frequencies, adiabatic and vertical excitation energies, and potential energy curves (PECs) as functions of the OSO bond angle and dissociation potential energy curves (DPECs) calculated using a Jacobi coordinate system. On the basis of our calculation results, we will assign the C, D, and E states of the SO_2^+ ion and discuss some aspects of dissociation of the C, D, and E states.

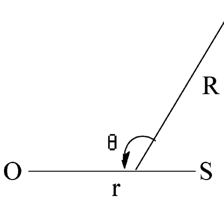

Figure 1. Jacobi coordinate system for the SO_2^+ ion used in the dissociation potential energy curve calculations (the r and θ parameters being fixed at the values of 1.4489 Å and 120°, respectively).

II. Calculation Details

We calculated in total 11 electronic states of the SO_2^+ ion, and they are as follows: the three lowest lying states in each of the A_1 (X^2A_1, 2^2A_1, and 3^2A_1), B_2 (1^2B_2, 2^2B_2, and 3^2B_2), and B_1 (1^2B_1, 2^2B_1, and 3^2B_1) symmetries and the two lowest lying states in the A_2 symmetry (1^2A_2 and 2^2A_2). In the present work, we will mainly study the eight high-lying electronic states of the SO_2^+ ion: 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, 1^2B_1, 2^2B_1, 3^2B_1, and 2^2A_2 (we call them as "the eight excited states" in the rest part of the present paper).

The CASSCF and CASPT2 calculations were carried out using the MOLCAS 5.2 quantum-chemistry software.[16] With a CASSCF wave function constituting the reference function the CASPT2 calculations were performed to compute the first-order wave function and the second-order energy in the full-CI space. In the calculations, we used two contracted atomic natural orbital (ANO) basis sets,[17−19] S[6s4p3d1f]/O[5s3p2d1f] and S[4s3p2d]/O[3s2p1d], denoted as ANO-L and ANO-S, respectively.

The equilibrium geometries for the 11 states were predicted by performing the CASSCF/ANO-L geometry optimization calculations, and the v_1 and v_2 vibrational frequencies in these states were calculated at the CASSCF/ANO-L level. The calculated geometries and frequencies for the X^2A_1, 1^2B_2, and 1^2A_2 states were already presented in our previous paper.[9] Based on the CASPT2/ANO-L energy values for the X^2A_1 state and for the eight excited states calculated at the respective CASSCF/ANO-L optimized geometries, we obtained the CASPT2/ANO-L//CASSCF/ANO-L adiabatic excitation energy (T_0) values for the eight excited states. Based on the CASPT2/ANO-L energy values for the X^2A_1 state and for the eight excited states calculated at the CASSCF/ANO-L geometry [r(S−O) = 1.439 Å and ∠OSO = 127.7°] of the X^2A_1 state,[9] we obtained the CASPT2/ANO-L//CASSCF/ANO-L vertical excitation energy (T_v) values for the eight excited states. Based on the CASPT2/ANO-L energy values for the X^2A_1 state and for the eight excited states calculated at the experimental geometry [R(S−O) = 1.432 Å and ∠OSO = 119.5°] of the ground-state SO_2 molecule,[20] we obtained the CASPT2/ANO-L relative energy (denoted as T_v') values of the eight excited states to the X^2A_1 state of the ion.

The PECs of the 11 states, $E(\angle OSO)$, as functions of the OSO bond angle (ranging from 60° to 180°) were calculated at the CASPT2/ANOS level, and in the curve calculations the S−O bond length value was fixed at 1.4489 Å, which is the bond length value in the CASSCF/ANO-S-optimized geometry for the X^2A_1 state. The X^2A_1, 1^2B_2, and 1^2A_2 PECs were already given in our previous paper.[9]

In exploring dissociation processes of the SO_2^+ ion in different electronic states to the product consisting of the SO^+ (SO) and O (O^+) species, a Jacobi coordinate system shown in Figure 1 was adopted to appropriately treat variations of the potential energies when one of the two S−O bonds is elongated

TABLE 2: Geometries[a] and the υ_1 and υ_2 Vibrational Frequencies for the Eight Excited States of the SO_2^+ Ion Predicted at the CASSCF/ANO-L Level

			frequencies (cm^{-1})		
state	*r* (S−O) (Å)	∠OSO (deg)	υ_1	υ_2	experimental frequencies (cm^{-1})
1^2B_1	1.593	109.2	788	370	*C* [b]: υ_1, 767 (782, 816, 807); υ_2, 409 (363, 375)
2^2B_1	1.609	94.1	822	570	*C* [c]: υ_1, 806; υ_2, 381
2^2A_2	1.626	95.8	822	375	*D* [b]: υ_1, ∼955; υ_2, ∼411
2^2A_1	1.533	118.4	908	374	*D* [d]: $-\upsilon_2$, ∼240
3^2A_1	1.564	108.1	1213	431	*E*[c]: υ_1, 960; υ_2, 444
2^2B_2	1.557	101.0	994	377	
3^2B_2	1.551	108.7	1216	429	
3^2B_1	1.589	110.7	728	332	

[a] In the text we refer to these optimized geometries as predicted "equilibrium geometries". [b] See Table 2 in ref 7. [c] Reference 3. [d] Reference 8.

TABLE 3: CASPT2/ANO-L Adiabatic (T_0) and Vertical (T_v) Excitation Energies of the Eight Excited States of the SO_2^+ Ion Calculated Using the CASSCF/ANO-L Optimized Geometries and the CASPT2/ANO-L Relative Energies (T_v') Calculated at the Experimental Geometry of the Ground-State SO_2 Molecule, Together with the Most Important Configurations (MICs) in the CASSCF Wave Functions Represented as the Ionized States of the Ground-State SO_2 Molecule

		T_0 (eV)							
state	MIC[a]	calcd	exptl[d]	state	MIC[a]	$T_v'^{b}$ (eV)	state	MIC[a]	T_v^{c} (eV)
X^2A_1	$(8a_1)^{-1}$	0.00[e]		X^2A_1	$(8a_1)^{-1}$	0.00[f]	X^2A_1	$(8a_1)^{-1}$	0.00[e]
1^2B_1	$(2b_1)^{-1}$	3.56	C: 3.55	1^2B_1	$(2b_1)^{-1}$	3.96	1^2B_1	$(8a_1)^{-2}(3b_1)^1$	4.09
2^2B_1	$(5b_2)^{-2}(3b_1)1$	3.59		2^2A_1	$(7a_1)^{-1}$	4.11	2^2B_1	$(2b_1)^{-1}$	4.11
2^2A_2	$(8a_1)^{-1}(5b_2)^{-1}(3b_1)^1$	3.82		2^2B_1	$(8a_1)^{-2}(3b_1)^1$	4.19	2^2A_1	$(7a_1)^{-1}$	4.37
2^2A_1	$(7a_1)^{-1}$	3.90	D: 3.99	2^2B_2	$(4b_2)^{-1}$	4.22	2^2B_2	$(4b_2)^{-1}$	4.51
3^2A_1	$(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1$	4.03		2^2A_2	$(8a_1)^{-1}(5b_2)^{-1}(3b_1)^1$	4.97	2^2A_2	$(8a_1)^{-1}(5b_2)^{-1}(3b_1)^1$	4.94
2^2B_2	$(8a_1)^{-1}(1a_2)^{-1}(3b_1)^1$	4.40	E: 4.16	3^2B_2	$(8a_1)^{-1}(1a_2)^{-1}(3b_1)^1$	5.42	3^2B_2	$(8a_1)^{-1}(1a_2)^{-1}(3b_1)^1$	5.59
3^2B_2	$(4b_2)^{-1}$	4.99		3^2A_1	$(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1$	6.04	3^2A_1	$(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1$	6.55
3^2B_1	$(8a_1)^{-2}(3b_1)^1$	5.25		3^2B_1	$(5b_2)^{-2}(3b_1)^1$	6.32	3^2B_1	$(5b_2)^{-2}(3b_1)^1$	6.92

[a] For the electron configuration of the ground-state SO_2 molecule; see the text or the footnote for Table 1. [b] Calculated at the experimental geometry [*r*(S−O) = 1.432 Å and ∠OSO = 119.5°] of the ground-state SO_2 molecule; see ref 20. [c] Calculated at the CASSCF/ANO-L geometry [*r*(S−O) = 1.439 Å and ∠OSO = 127.7°] of the X^2A_1 state of the SO_2^+ ion; see ref 9. [d] Evaluated using the experimental adiabatic ionization potential data reported in ref 2. [e] The CASPT2/ANO-L energy is −547.55403 au. [f] The CASPT2/ANO-L energy is −547.54409 au.

in the course of the dissociation. The distance *r* and angle θ in the Jacobi coordinate system (see Figure 1) were fixed at the values of 1.4489 Å (see the last paragraph) and 120°, respectively, and the DPECs, *E*(R), were calculated as functions of the parameter R (see Figure 1) at the CASPT2/ANO-S level.

Electronic states of the SO_2^+ ion at the linear geometry with the S−O bond length of 1.4489 Å (see above) were calculated at the CASPT2/ANO-S level. The calculations were carried out in the D_{2h} subgroup of $D_{\infty h}$, where Σ_g^+ corresponds to the A_g irreducible representation, Σ_u^+ to B_{1u}, Π_g to $B_{2g} + B_{3g}$, Π_u to $B_{2u} + B_{3u}$, Δ_g to $A_g + B_{1g}$, and Δ_u to $A_u + B_{1u}$.

In our CASSCF calculations, 11 electrons were active and the active space included 13 orbitals [CASSCF (11,13)]. The choice of this active space stemmed from the molecular orbital (MO) sequence for the ground-state SO_2 molecule. Based on the HF/6-31+G(d) calculations, the ground-state SO_2 molecule has the following electronic configuration (the twelve valence MOs with the occupancies given in increasing order of the MO energy): ......$(5a_1)^2(3b_2)^2(6a_1)^2(4b_2)^2(7a_1)^2(2b_1)^2(5b_2)^2(1a_2)^2(8a_1)^2(3b_1)^0(9a_1)^0(10a_1)^0$. Our active space was formed from the full-valence active space by deleting the $5a_1$, $3b_2$, and $6a_1$ MOs (the MO energy gap between $6a_1$ and $4b_2$ being larger than 5 eV) and by adding four virtual MOs ($6b_2$, $4b_1$, $11a_1$, and $7b_2$) lying above the $10a_1$ MO. Labeling the orbitals within the C_{2v} point group in the order of a_1, a_2, b_2, and b_1, this active space is named (5143). Labeling the orbitals within the C_s point group (in the calculations for the DPECs) in the order of a′ and a″, the active space is named (94). Labeling the orbitals within the D_{2h} point group (in the calculations for electronic states at the linear geometry) in the order of a_g, b_{3u}, b_{2u}, b_{1g}, b_{1u}, b_{2g}, b_{3g}, and a_u, the active space is named (23302210). In the CASSCF calculation steps of our CASPT2 calculations for T_v, T_v', *E*(∠OSO) PECs, *E*(R) DPECs, and electronic states at the linear geometry, the state-averaging technique was used, and the averaging includes all the states of interest for a given symmetry of the C_{2v}, C_s, or D_{2h} group. In all the CASPT2 calculations the weight (denoted as ω) values of the CASSCF reference functions in the first-order wave functions were larger than 0.74, unless otherwise noted.

III. Results and Discussion

In Table 2 are given the CASSCF/ANO-L-optimized geometries and the CASSCF/ANO-L υ_1 and υ_2 frequency values for the eight excited states, together with the experimental υ_1 and υ_2 values in the C, D, and E states of the SO_2^+ ion. In Table 3 are given the CASPT2/ANO-L//CASSCF/ANO-L T_0 and T_v values and the CASPT2/ANO-L T_v' values for the eight excited states, together with the experimental T_0 values for the C, D, and E states of the SO_2^+ ion.

The CASPT2/ANO-S *E*(∠OSO) PECs of the eight excited states are given in Figure 2. The CASPT2/ANO-S *E*(R) DPECs of the 1-6^2A′ and 1-5^2A″ states of SO_2^+ are given in Figure 3.

A. Equilibrium Geometries. The CASSCF/ANO-L-optimized geometries given in Table 2 are called as the predicted "equilibrium geometries" of the eight excited states of SO_2^+ in the rest of the present paper, and these predicted "equilibrium geometries" have OSO bond angles ranging from 94.1° to 118.4°. In section III.D we will mention other minimum energy geometries in the CASSCF/ANO-L potential energy surfaces (PESs) of the 1^2B_1, 2^2A_1, and 3^2A_1 states, but the OSO angles in those geometries are too small or too large (180°), compared to the OSO angles (see above) in the geometries of the ground-state molecule and ion.

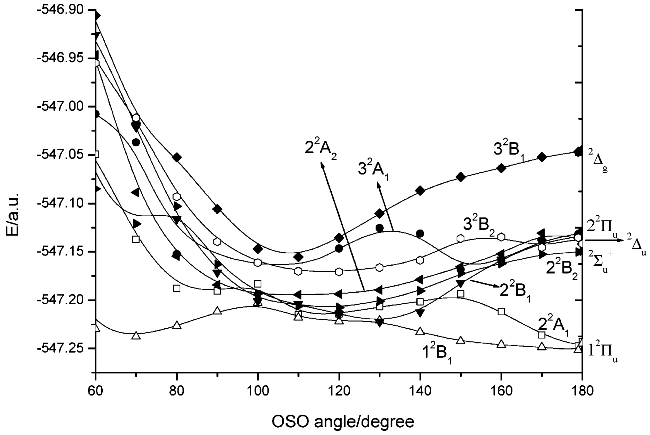

Figure 2. CASPT2/ANO-S potential energy curves [$E(\angle OSO)$] for the eight excited states of SO_2^+.

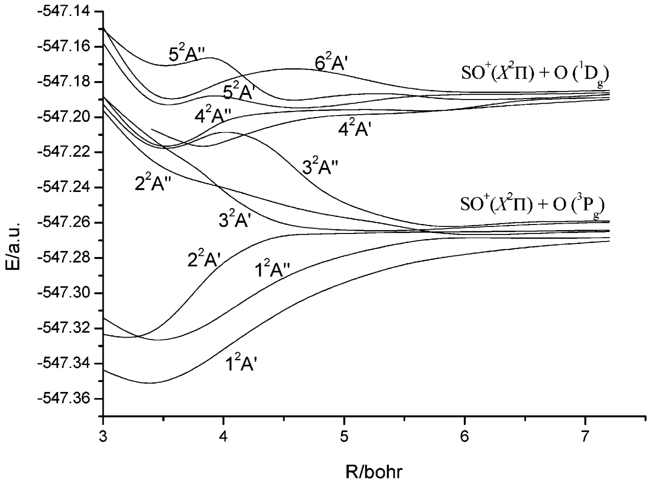

Figure 3. CASPT2/ANO-S dissociation potential energy curves [E(R)] for the 1−6 $^2A'$ and 1−5 $^2A''$ states of SO_2^+, calculated using the Jacobi coordinate system defined in Figure 1.

The S−O bond lengths in the CASSCF/ANO-L geometries of the eight excited states are longer than the bond length (1.432 Å) in the experimental geometry of the ground-state SO_2 molecule[20] and longer than the bond length (1.439 Å) in the CASSCF/ANO-L geometry of the ground-state SO_2^+ ion.[9] The OSO bond angles in the CASSCF/ANO-L geometries of the eight excited states are smaller than the angle (119.5°) in the experimental geometry of the ground-state SO_2 molecule[20] and smaller than the angle (127.7°) in the CASSCF/ANO-L geometry of the ground-state SO_2^+ ion.[9] In the CASSCF/ANO-L geometries of the 2^2B_1 and 2^2A_2 states the S−O bonds are very long (longer than 1.6 Å).

The CASSCF/ANO-L υ_1 and υ_2 frequency values in the eight excited states of SO_2^+ will be compared with the experimental υ_1 and υ_2 values in the C, D, and E states, when we consider the assignments of the observed C, D, and E states (see below).

B. Energy Orderings and Characters of the Eight Excited States. The CASPT2/ANO-L T_0, T_v', and T_v orderings for the eight excited states of the SO_2^+ ion are given in columns 1, 5, and 8, respectively, of Table 3, and apparently the T_0, T_v', and T_v orderings are different. The CASPT2/ANO-L T_0 ordering of the eight excited states is the most important, and it reads: 1^2B_1, 2^2B_1, 2^2A_2, 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, 3^2B_1 (in increasing order of the T_0 energy).

We characterize the eight excited states by checking the most important configurations (MICs) in their CASSCF/ANO-L wave functions. The MICs for the eight excited states in the T_0, T_v', and T_v energy orderings are represented as "primary ionization configurations" or "shake-up ionization configurations" with respect to the electronic configuration (see section II) of the ground-state SO_2 molecule, and they are given in columns 2, 6, and 9 of Table 3. Though some of the eight excited states have different MICs in the different orderings (i.e., at the different geometries), we could find only eight different MICs in columns 2, 6, and 9 of Table 3, and they are three primary and five shake-up ionization configurations. The three primary ionization configurations involve the occupied $2b_1$, $7a_1$, and $4b_2$ MOs of the SO_2 molecule, and the five shake-up ionization configurations involve the lowest unoccupied MO ($3b_1$) and one or two of the three highest occupied MOs ($5b_2$, $1a_2$, and $8a_1$) of the SO_2 molecule.

Since the geometries of the ground-state molecule and ion are not far different (only the OSO angle values being significantly different, see above), the T_v' and T_v orderings are the same except that 2^2A_1 and 2^2B_1 interchange in the two orderings, which implies a 2^2A_1−2^2B_1 PES crossing. The MICs for 1^2B_1 and 2^2B_1 interchange in the T_v' and T_v orderings, which implies an 1^2B_1-2^2B_1 PES avoided-crossing. Since the equilibrium geometries of the eight excited states are quite different from the geometries of the ground-state molecule and ion, the T_0 ordering is quite different from the T_v' and T_v orderings, which implies PES crossings. In the T_0 and T_v' orderings, the MICs for 2^2B_1 and 3^2B_1 interchange and the MICs for 2^2B_2 and 3^2B_2 interchange, which implies 2^2B_1-3^2B_1 and 2^2B_2-3^2B_2 PES avoided-crossings.

C. Assignments of the C, D, and E States. Reliable assignment of an observed state (C, D, or E) to a calculated state should be based on the reasonable agreements of the calculated T_0 and frequency values with the experimental values. Furthermore, we would think that the C, D, and E states should be preferably assigned to the calculated states having primary ionization character at the molecular geometry (i.e., in the T_v' ordering) since they were detected in the photoelectron spectra of the molecule.[2,3]

We assign the C state of the SO_2^+ ion to 1^2B_1, which is the first (the lowest-lying) state in the T_0 ordering of the eight excited states (see section III.B or Table 3). This assignment is based on the facts that the CASPT2/ANO-L//CASSCF/ANO-L T_0 value of 3.56 eV for 1^2B_1 is very close to the experimental T_0 value of 3.55 eV for the C state[2] and that the CASSCF/ANO-L υ_1 and υ_2 values of 788 and 370 cm^{-1} for 1^2B_1 are respectively close to the experimental υ_1 and υ_2 values of 767 and 409 cm^{-1} (see Table 2) for the C state reported by Thomas et al.[7] The calculated υ_1 and υ_2 values are also close to the experimental values (see Table 2) reported by the other groups.[3,7] The deviations of the calculated frequency values from the experimental values are smaller than 40 cm^{-1}. The 1^2B_1 state has a primary ionization character [$(2b_1)^{-1}$] at the molecular geometry and at its equilibrium geometry (see Table 3). Our assignment of the C state is the same as the assignment (to $^2B_1$) by Hillier and Saunders[10] and by Thomas et al.,[7] but it is different from the assignment (to $^2A_1$) by Zhang et al.[8] and from the assignment (to $^2B_2$) by Wang et al.,[2] Holland et al.,[3] and Dujardin and Leach.[5] The calculated T_0 value (see Table 3) for 2^2B_1 is also very close to the experimental T_0 value for the C state. However, the calculated υ_2 value of 570 cm^{-1} for 2^2B_1 is much larger than the experimental υ_2 value, and the 2^2B_1 state has a shake-up ionization character at the molecular geometry [$(8a_1)^{-2}$ $(3b_1)^1$] and at its equilibrium geometry [$(5b_2)^{-2}$ $(3b_1)^1$].

We assign the D state of the SO_2^+ ion to 2^2A_1, which has a primary ionization character [$(7a_1)^{-1}$] at the molecular geometry and at its equilibrium geometry (see Table 3). In the T_0 ordering (see section III.B) there are the 2^2B_1 and 2^2A_2 states between 1^2B_1 and 2^2A_1, but the 2^2B_1 and 2^2A_2 states have shake-up ionization characters at the molecular geometry and at their equilibrium geometries (see Table 3). The CASPT2/ANO-L//CASSCF/ANO-L T_0 value of 3.90 eV for 2^2A_1 is very close to the experimental T_0 value of 3.99 eV for the D state.[2] The CASSCF/ANO-L υ_1 and υ_2 values of 908 and 374 cm^{-1} for 2^2A_1 are, respectively, in reasonable agreement with the experimental υ_1 and υ_2 values of 955 and 411 cm^{-1} for the D state observed by Thomas et al.[7] (the deviations being smaller than 50 cm^{-1}). Our assignment for the D state is the same as the assignment (to $^2A_1$) by Hillier and Saunders,[10] Wang et al.,[2] Holland et al.,[3] and Dujardin and Leach,[5] but it is different from the assignment (to $^2B_1$) by Zhang et al.[8] and the assignment (to $^2B_2$) by Thomas et al.[7] Zhang et al.[8] recently observed a υ_2 value of 240 cm^{-1} for the *D* state, which is 170 cm^{-1} smaller than the observed υ_2 value of Thomas et al.[7] In the CASSCF/ANO-L (υ_1 and υ_2) frequency calculations for all the eight excited states we have not got any frequency values smaller than 330 cm^{-1} (see Table 2). We will try to understand the experiments of Zhang et al.[8] in the future.

In the T_0 ordering (see section III.B), the 3^2A_1, 2^2B_2, 3^2B_2, and 3^2B_1 states follow the 2^2A_1 state, and we intend to assign the E state of the SO_2^+ ion to 2^2B_2. Though the 2^2B_2 state has a shake-up ionization character $[(8a_1)^{-1}\ (1a_2)^{-1}\ (3b_1)^1]$ at its equilibrium geometry, it has a primary ionization character $[(4b_2)^{-1}]$ at the molecular geometry. The CASPT2/ANO-L//CASSCF/ANO-L T_0 value of 4.40 eV for 2^2B_2 is 0.24 eV larger than the experimental T_0 value of 4.16 eV for the E state.[2] The CASSCF/ANO-L υ_1 value of 994 cm^{-1} for 2^2B_2 is 34 cm^{-1} larger than the experimental υ_1 value for the E state reported by Holland et al.,[3] and the CASSCF/ANO-L υ_2 value of 377 cm^{-1} for 2^2B_2 is 67 cm^{-1} smaller than the experimental υ_2 value [3] (see Table 2). The deviations of 0.24 eV and 67 cm^{-1} for T_0 and υ_2, respectively, are somewhat large. However, we think that our calculated T_0 and frequency values for 2^2B_2 are still in reasonable agreement with the respective experimental values for the E state. Our assignment of the E state to 2^2B_2 is the same as the assignment (to $^2B_2$) by Hillier and Saunders[10] and by Zhang et al.,[8] but it is different from the assignment (to $^2B_1$) by Wang et al.,[2] Holland et al.,[3] and Dujardin and Leach.[5]

The CASPT2/ANO-L//CASSCF/ANO-L T_0 value of 4.03 eV for 3^2A_1 is quite close to the experimental T_0 value for the E state. However, the CASSCF/ANO-L υ_1 value (see Table 2) for 3^2A_1 is much larger than the experimental υ_1 value for the E state, and the 3^2A_1 state has a shake-up ionization character $[(1a_2)^{-1}\ (5b_2)^{-1}\ (3b_1)^1]$ at the molecular geometry and at its equilibrium geometry. The 3^2B_2 state has a primary ionization character at its equilibrium geometry, but it has a shake-up ionization character at the molecular geometry. The 3^2B_1 state has a shake-up ionization character at the molecular geometry and its equilibrium geometry (having different MICs at the two geometries). The CASPT2/ANO-L//CASSCF/ANO-L T_0 values for 3^2B_2 and 3^2B_1 (4.99 and 5.25 eV, respectively) are much larger than the experimental T_0 value for the E state.

We also performed calculations for the 4^2A_1, 4^2B_2, and 3^2A_2 states. Our CASPT2/ANO-L//CASSCF/ ANO-L T_0 calculations indicate that the 4^2A_1 and 4^2B_2 states are higher in energy than 3^2B_1 while the 3^2A_2 state is lower than 3^2B_1 (and lower than 3^2B_2). However, the calculated T_0 value of 4.84 eV for 3^2A_2 is much larger than the experimental T_0 value for the E state.

D. Potential Energy Curves as Functions of the OSO Angle. The purpose of computing the $E(\angle OSO)$ [r(S−O) = 1.4489 Å] PECs for the electronic states of the SO_2^+ ion is for preliminarily exploring the PESs. The CASPT2/ANO-S PECs for the eight excited states are shown in Figure 2. We will first describe correlation relations between the C_{2v} states and the $D_{\infty h}$ states at the linear geometry. Our CASPT2/ANO-S calculations at the linear geometry [r(S−O) = 1.4489 Å] predict that the $^2\Sigma_g^+$, $1^2\Pi_u$, $^2\Pi_g$, $^2\Sigma_u^+$, $^2\Delta_u$, $2^2\Pi_u$, and $^2\Delta_g$ states are the seven lowest lying states (in an increasing order of energy) of SO_2^+ at the linear geometry (the $^2\Delta_u$ state was erroneously labeled $^2\Gamma_u$ in ref 9). It was already stated in our previous paper[9] that the 1^2A_1 state correlates with $^2\Sigma_g^+$ and the 1^2B_2 and 1^2A_2 states converge to $^2\Pi_g$. When the OSO angle value increases to 180°, the 1^2B_1 and 2^2A_1 states converge to $1^2\Pi_u$; the 3^2B_2 and 2^2A_2 states converge to $^2\Delta_u$; and the 2^2B_1 and 3^2A_1 states converge to $2^2\Pi_u$. These three pairs of states are considered as the results of the Renner−Teller effect in the three degenerate states ($1^2\Pi_u$, $^2\Delta_u$, and $2^2\Pi_u$) at the linear geometry. The 2^2B_2 and 3^2B_1 states correlate with the $^2\Sigma_u^+$ and $^2\Delta_g$ states, respectively [there should be one more higher-lying state (4^2A_1) correlating with $^2\Delta_g$].

There are unique minima along the $E(\angle OSO)$ PECs of the 2^2A_2, 2^2B_2, 3^2B_2, and 3^2B_1 states shown in Figure 2, and the minima are located at the OSO angle values of around 100°, 105°, 108°, and 107°, which are not far from the OSO angle values in the CASSCF/ANO-L equilibrium geometries of the respective states given in Table 2.

Along the 1^2B_1 PEC, we found three minima at the OSO angle values of around 65°, around 110°, and 180°, implying three minima in the 1^2B_1 PES. The minimum at the angle value of around 110° along the PEC should correspond to the minimum at the 1^2B_1 equilibrium geometry [r(S−O) = 1.593 Å and $\angle$OSO = 109.2°] in the PES. By performing full-geometry optimization calculations we found other two minima in the CASSCF/ANO-L PES of the 1^2B_1 state, one at a bent geometry [r(S−O) = 1.600 Å and $\angle$OSO = 60.8°] and the other at a linear geometry [r(S−O) = 1.496 Å and $\angle$OSO = 180°], and the CASPT2/ANO-L energies at these two geometries are slightly lower than that at the CASSCF/ANO-L equilibrium geometry given in Table 2. However, the OSO angle values in these two extra geometries are far from the angle values in the geometries of the ground-state molecule (119.5°) and ion (127.7°), and these two extra minima are far away from the Franck−Condon regions for the ground-state molecule and ion.

Along the 2^2B_1 PEC, we found one minimum at the OSO angle value of around 130°. We performed the CASSCF/ANO-L full geometry optimization calculations with a trial geometry having a bond angle of 130°, and we got an optimized geometry identical to the CASSCF/ANO-L equilibrium geometry of the 2^2B_1 state, which indicates that the equilibrium geometry given in Table 2 is the unique minimum-energy geometry in the CASSCF/ANO-L PES of the 2^2B_1 state.

Along the 2^2A_1 PEC, we found three minima at the OSO angle values of ∼85°, ∼115°, and 180°, implying three minima in the 2^2A_1 PES. The minimum at the angle value of around 115° along the PEC should correspond to the minimum at the 2^2A_1 equilibrium geometry [r(S−O) = 1.533 Å and $\angle$OSO = 118.4°] in the PES. By performing full-geometry optimization calculations we found other two minima in the CASSCF/ANO-L PES of the 2^2A_1 state, one at a bent geometry [r(S−O) = 1.617 Å and $\angle$OSO = 83.2°] and the other at a linear geometry [r(S−O) = 1.496 Å and $\angle$OSO = 180°]. The CASPT2/ANO-L energy at the bent geometry is higher than that at the CASSCF/ANO-L equilibrium geometry given in Table 2, while the energy at the linear geometry is lower than that at the equilibrium geometry. However the linear geometry is far away from the Franck−Condon regions for the ground-state molecule and ion.

Along the 3^2A_1 PEC, we found two minima at the OSO angle values of around 105° and around 155°. The minimum at the angle value of around 105° along the PEC should correspond to the minimum at the 3^2A_1 equilibrium geometry [r(S−O) = 1.564 Å and ∠OSO = 108.1°] in the PES. By performing full-geometry optimization calculations we found another minimum in the CASSCF/ANO-L PES of the 3^2A_1 state at a slightly bent geometry [r(S−O) = 1.598 Å and ∠OSO = 160.6°]. However, the CASPT2/ANO-L energy at this geometry is higher than that at the CASSCF/ANO-L equilibrium geometry given in Table 2.

Many PES crossings and PES avoided-crossings can be detected in Figure 2. We will only mention the PES avoided-crossings. The 1^2B_1-2^2B_1, 2^2B_1-3^2B_1, and 2^2B_2-3^2B_2 PES avoided-crossings occur in the geometric regions with the OSO angle values of around 130°, 70°, and 85°, respectively. The two 2^2A_1-3^2A_1 PES (PEC) avoided-crossings occur at the OSO angle values of around 100° and 150°. Interchanges of the MICs in each pair of the states were detected at the respective PES avoided-crossing regions (at the respective OSO angle values).

E. Dissociation Potential Energy Curves. Dynamic studies[2−6,11] indicate that the C, D, and E states of the SO_2^+ ion could predissociate to the first product limit, SO^+ ($X^2\Pi$) + O (^3P_g). In the course of the dissociation the SO_2^+ system has C_s symmetry. By using the Jacobi coordinate system (C_s symmetry) shown in Figure 1, the CASPT2/ANO-S DPECs, E(R) (r = 1.4489 Å and θ = 120°; and R ranging from 3.0 to 7.2 bohr), for the 1-$6^2A'$ and 1-$5^2A''$ states of the SO_2^+ ion were calculated, and the DPECs are shown in Figure 3. The CASPT2 calculations for $4^2A'$ were not successful at small R values due to small weight values of the CASSCF reference functions. The predissociation processes are usually complicated. In the present study, we will only try to theoretically determine the C_{2v} states correlating to the first product limit. For this purpose, we have to determine first the C_s states which are related to the first product limit and then the C_{2v} states those C_s states correlate with.

We could simply determine the C_s states related to the first product limit based on our DPEC calculations. As shown in Figure 3, the $1^2A'$, $2^2A'$, $3^2A'$, $1^2A''$, $2^2A''$, and $3^2A''$ DPECs converge to the first product limit [SO^+ ($X^2\Pi$) + O (^3P_g)]. According to Dujardin and Leach, combination of SO^+ ($X^2\Pi$) and O (^3P_g) is related to six doublet states in the C_s symmetry: three $^2A'$ and three $^2A''$ (the three $^2A'$ states will correlate with three $^2A_1$ and/or $^2B_2$ C_{2v} states and the three $^2A''$ states with three $^2B_1$ and/or $^2A_2$ C_{2v} states).[5] Our DPEC calculation results support the consideration of Dujardin and Leach.

The Jacobi coordinate system at the R value of 3.0 bohr has a geometry approximately equivalent to a C_{2v} geometry with an OSO bond angle of 103° [r(S−O) = 1.4489 Å]. We performed the CASPT2/ANO-S calculations at the C_{2v} geometry [r(S−O) = 1.4489 Å and ∠OSO = 103°] using the C_{2v} and C_s symmetries, and we tried to determine the state-to-state correlation relations between the C_{2v} and C_s states by comparing the CASPT2/ANO-S energies of the calculated C_{2v} and C_s states. However, we found that, for high-lying states, there were discrepancies between the energy values calculated using the C_{2v} and C_s symmetries (probably due to technical problems), and it would be difficult to determine state-to-state correlation relations for the high-lying states which are close in energy. We can determine the following state-to-state correlation relations: $1^2A'$ to 1^2B_2, $2^2A'$ to 1^2A_1, $1^2A''$ to 1^2A_2, and $2^2A''$ to 1^2B_1. Since the $3^2A'$, $4^2A'$, $3^2A''$, and $4^2A''$ states are very close in energy at R = 3.0 bohr in Figure 3 (equivalent to the fact that the 2^2A_1, 2^2B_2, 2^2B_1, and 2^2A_2 states are very close in energy at ∠OSO = 103° in Figure 2), we are not able to determine if the $3^2A'$ state corresponds to 2^2A_1 or 2^2B_2 either and if the $3^2A''$ state corresponds to 2^2B_1 or 2^2A_2 either.

Based on the arguments presented in the last two paragraphs, we can determine that the 1^2A_1 ($2^2A'$), 1^2B_2 ($1^2A'$), 1^2A_2 ($1^2A''$), and 1^2B_1 ($2^2A''$) states correlate to the first product limit, SO^+ ($X^2\Pi$) + O (^3P_g). Based on the assignments presented in our previous[9] and present papers, we conclude that the X (X^2A_1), A (A^2B_2), B (B $^2A_2$), and C (C $^2B_1$) states of the SO_2^+ ion correlate to the first product limit. We can also say that either 2^2A_1 or 2^2B_2 state correlates to the first product limit and that either 2^2B_1 or 2^2A_2 state correlates to the first product limit [both 2^2B_1 and 2^2A_2 have shake-up ionization character at the molecular geometry and at their equilibrium geometry (see Table 3)]. We have assigned the D state of the SO_2^+ ion to 2^2A_1 and the E state to 2^2B_2. These arguments indicate that, among the C, D, and E states, only two correlate to the first product limit. This fact might be already known by the experimental groups (those listed in Table 1) since, among the six C_{2v} states to which the X, A, B, C, D, and E states were assigned, there were always four states corresponding to the $^2A'$ states, though the different groups suggested the different assignments for the C, D, and E states (see Table 1).

The CASPT2/ANO-S energy difference between the 2 $^2A'$ state at R = 7.2 bohr and the X^2A_1 state at the equilibrium geometry is evaluated to be 2.6 eV, which is about 1 eV smaller than the experimental dissociation energy value of ∼3.6 eV. [7] Accurate prediction of dissociation energies is usually difficult. We note that the dissociation energy of the ground-state SO_2 molecule (into SO + O) calculated at the MRCI/cc-pVDZ level [21] was about 1.4 eV smaller than the experimental value. However, the energy separation between the two asymptote product groups (see Figure 3) is evaluated to be about 2 eV, which is close to the experimental value between the first and second limits (see ref 5 and references therein).

IV. Conclusions

For exploring the *C, D, and E* states of the SO_2^+ ion, eight excited states of SO_2^+, 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, 1^2B_1, 2^2B_1, 3^2B_1, and 2^2A_2, have been calculated using the CASSCF and CASPT2 methods in conjunction with the ANO-S and ANO-L basis sets (the 1^2A_1, 1^2B_2, and 1^2A_2 states were previously calculated and assigned to the X, A, and B states of SO_2^+, respectively).

For the eight excited states, geometries were optimized and the v_1 and v_2 vibrational frequencies were calculated at the CASSCF/ANO-L level. The optimized geometries of the eight excited states given in Table 2 are called "equilibrium geometries", and the OSO bond angles in these geometries range from 94.1° to 118.4°. The CASPT2/ANO-L adiabatic excitation energy (T_0) values and vertical excitation energy (T_v) values for the eight excited states were calculated using the CASSCF/ANO-L optimized geometries. The CASPT2/ANO-L relative energy (T_v') values of the eight excited states to X^2A_1 were calculated at the experimental geometry of the ground-state SO_2 molecule. Our calculations predict the following T_0 ordering for the eight excited states: 1^2B_1, 2^2B_1, 2^2A_2, 2^2A_1, 3^2A_1, 2^2B_2, 3^2B_2, and 3^2B_1 (in increasing order of energy). The T_v and T_v' orderings are quite different from the T_0 ordering. By checking the most important configurations (MICs) in the CASSCF/ANO-L wave functions we characterize the eight excited states in the T_0, T_v, and T_v' orderings as primary and shake-up ionization states. Some of the states have different MICs in the different orderings.

Different assignments of the C, D, and E states of the SO_2^+ ion were previously suggested by different groups. We assign the C, D, and E states of the SO_2^+ ion to 1^2B_1, 2^2A_1, and 2^2B_2, respectively. The CASPT2/ANO-L T_0 values and the CASSCF/ANO-L ν_1 and ν_2 values for the 1^2B_1 and 2^2A_1 states are in good agreement with the experimental T_0, ν_1, and ν_2 values for the C and D states, respectively. The 1^2B_1 and 2^2A_1 states have primary ionization character [the MICs being represented as $(2b_1)^{-1}$ and $(7a_1)^{-1}$, respectively] at the molecular geometry and at their equilibrium geometries. The CASPT2/ANO-L T_0 value and the CASSCF/ANO-L ν_1 and ν_2 values for the 2^2B_2 state are in reasonable agreement with the experimental T_0, ν_1, and ν_2 values for the E state, respectively. The 2^2B_2 state has a primary ionization character $[(4b_2)^{-1}]$ at the molecular geometry.

For preliminarily exploring the PESs, the $E(\angle OSO)$ PECs of the eight excited states were calculated at the CASPT2/ANO-S level. The general features of the PECs imply that some of the states may have other minimum energy geometries in their PESs than the equilibrium geometries given in Table 2. By performing the CASSCF/ANO-L full-geometry optimization calculations we found two and one extra minimum energy geometries in the 1^2B_1 and 2^2A_1 PESs, respectively, which have lower CASPT2/ANO-L energies than the equilibrium geometries of the respective states. However, these extra minimum energy geometries have either too small (60.8°) or too large (180°) OSO angles and they are far away from the Franck−Condon regions for the ground-state molecule and ion.

For preliminarily exploring dissociation processes of the SO_2^+ ion into the first product limit [SO^+ (SO) + O (O^+)], we adopted a Jacobi coordinate system and calculated the CASPT2/ANO-S DPECs, E(R), for the 1-$6^2A'$ and 1-$5^2A'$ states. The calculation results (shown in Figure 3) indicate that the $1^2A'$, $2^2A'$, $3^2A'$, $1^2A''$, $2^2A''$, and $3^2A''$ DPECs converge to the first product limit. By considering the state-to-state correlation relations between the C_{2v} and C_s states and our assignments for the C, D, and E states, we conclude that the C state correlates to the first product limit and that, among the D and E states, only one correlates to the first product limit.

Acknowledgment. This work was supported by the National Natural Science Foundation Committee of China (No. 20173056, 20333050) and the Ministry of Science and Technology of China (No. G1999075300). We thank Profs. L. Zhang and S. Yu for helpful discussions.

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