Vibronic theory for the x-ray absorption spectrum of CF$_4$ molecules

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The C $1s$ x-ray absorption spectrum of CF$_4$ molecules is theoretically investigated by calculating the line shape quantum mechanically based upon a vibronic model. It is found that the main peak with a broad width is attributed to the transition of the C $1s$ core electron to the antibonding valence orbitals which are coupled with the C—F bond-stretching modes through the Jahn-Teller and the quasi-Jahn-Teller interactions. It is also clarified that the sharp asymmetric absorption line at the higher-energy side of the main band comes from the transition to the Rydberg states, where the interference effect between the Rydberg states and the vibronic state of the antibonding molecular orbitals leads to the asymmetric structure. [S1050-2947(99)09312-9]

I. INTRODUCTION

Recent advances in the techniques of synchrotron radiation as an intense light source opened a new stage in soft-x-ray spectroscopy. The dramatic improvement of spectral resolution in the x-ray absorption spectrum has enabled us to observe fine structures such as vibrational side bands, which have been smeared out by the instrumental broadening so far. Since the discovery of the vibrational structures in the core absorption spectrum in the N$_2$ molecule by Chen *et al.* [1], many experimental works have been carried out on the vibrational excitations in the x-ray absorption processes of molecules [2]. Recently, Ueda *et al.* have experimentally investigated C $1s$ absorption spectra of CH$_4$, CH$_3$F, CH$_2$F$_2$, CH$_3$F, and CF$_4$, and found that the spectral shape is systematically changed as a hydrogen atom is substituted by a fluorine atom one by one [3]: A broad absorption band emerges below sharp Rydberg transition lines as the number of the fluorine atoms increases. This broad absorption band has been assigned to the transition to the antibonding valence orbitals. The large width of the absorption band suggests that the molecular vibrations are highly excited by strong vibronic couplings in the core excited state.

The experimental result obtained by Ueda *et al.* is shown in Fig. 1 [3]. Essentially the same result has been obtained also by Itchkawitcz *et al.* [4]. The broad absorption band below 299.3 eV is assigned to the transition from C $1s$ to the antibonding $\sigma^*(t_2)$ state [5], and the sharp peaks appearing in the region from 299.3 eV to the ionization threshold are attributed to the transition to the Rydberg states. The broadband has a peculiar feature of a shoulder in the lower-energy side of the main absorption peak, while a distinct dip appears on the higher-energy side. It is speculated that the spectral line shape of the main band may be due to the Jahn-Teller splitting of $\sigma^*(t_2)$ states with threefold degeneracy [6]. However, there has been no quantitative analysis of the spectral shape. In particular, although the dipole forbidden valence orbital state $\sigma^*(a_1)$ does exist around the $\sigma^*(t_2)$ states, no attention has been paid to the significance of the $\sigma^*(a_1)$ state. On the other hand, the several Rydberg transition lines have been interpreted as originating from the transition to npt_2 and ndt_2 states accompanied by the vibrational side bands of the breathing mode [3]. But the dip structure between the broad absorption band and the Rydberg transition lines has not been fully discussed.

The molecular deformation induced by the core excitation is one of the recent topics in soft-x-ray spectroscopy [7]. Since the pioneering work by Morin *et al.* [8], it has been revealed that atomic displacement leading to a specific mode of molecular dissociation is triggered by the resonant excitation of the core electron to antibonding molecular orbitals in a number of simple molecules [9,10]. Relatively long lifetimes of the core hole in light elements make it possible for the molecule to deform before Auger decay. Also in CF$_4$, it has been found that a certain channel of molecular dissociation is enhanced by a resonant core excitation, which indicates that a specific mode of deformation is induced in the core-excited state. In order to understand the mechanism of the ultrafast molecular deformation in the core-excited states,
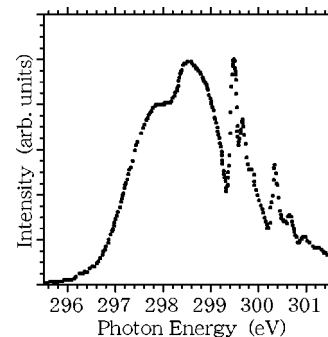

FIG. 1. The experimental results of the high resolution C $1s$ x-ray absorption spectrum of the CF$_4$ molecule [3].
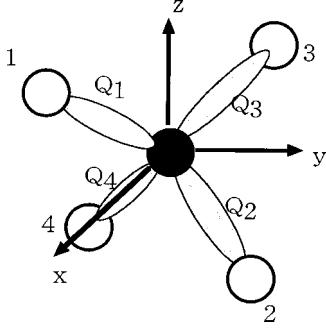
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FIG. 2. The molecular structure of CF_4 with T_d symmetry. Closed and open circles represents C atom and F atoms, respectively. Q_i $(i=1-4)$ represent four stretching mode of C—F bonds.

it is important to obtain information on the vibronic couplings as well as on the electronic energy levels in the excited states.

The aim of the present paper is to clarify the spectral features of C $1s$ absorption of a CF_4 molecule by a relatively simple vibronic coupling model. A full quantum-mechanical calculation of the absorption spectrum is carried out for a vibronic model, in which not only the Jahn-Teller coupling within the subspace of $\sigma^*(t_2)$ states but also the quasi-Jahn-Teller coupling between the $\sigma^*(a_1)$ and $\sigma^*(t_2)$ states is taken into account. It will be shown that the experimental result of the C $1s$ absorption spectrum of CF_4 is successfully reproduced by an appropriate choice of a set of parameter values in our theoretical model. It is found that the C $1s$ electron is excited also to the a_1 state with the help of the quasi-Jahn-Teller coupling, and this effect plays a crucial role in determining the structure of the main band. Furthermore, we also consider the transition to the Rydberg states, which are assumed to be hybridized with the valence orbitals through the configuration interaction. This hybridization causes the interference between the two transitions, one to the vibronically broadened molecular orbitals and the other to the sharp Rydberg states, and results in the dip structure.

In Sec. II, the model used here is presented. The calculated results are shown in Sec. III together with discussions, and concluding remarks are given in Sec. IV.

II. MODEL

The CF_4 molecule has a tetrahedral structure belonging to the T_d symmetry group as shown in Fig. 2. The ground-state electronic configuration of molecular orbitals in CF_4 is

$$(\text{core}) \ 1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1^6; 4t_2^0 3a_1^0.$$

The Rydberg states exist in an energy region higher than the molecular orbitals. By x-ray irradiation, a C $1s$ core electron is excited to unoccupied molecular orbitals $4t_2$ and $3a_1$. These states consist of the four equivalent antibonding orbitals between C sp^3 hybridized orbitals and F $2p$ orbitals, so the $4t_2$ and $3a_1$ states are equivalent to the $\sigma^*(t_2)$ and $\sigma^*(a_1)$ states mentioned in Sec. I, respectively. We denote the $4t_2$ and $3a_1$ states as $|t_{2i}\rangle$ $(i=x,y,x)$ and $|a_1\rangle$, respectively, and hereafter we use the abbreviation of t_2 for the former state and a_1 for the latter state.

In addition to these molecular orbitals, we consider also p-like Rydberg states denoted as $|p_i\rangle$ $(i=x,y,z)$. These states correspond to the lower series of the sharp transition lines in Fig. 1. The higher one may be assigned to the transition to d-like states, but we neglect them for simplicity, because the structure can be understood essentially as a replica of the p-like states.

Because of the antibonding character of the molecular orbitals, the core excited states are strongly coupled with the molecular vibrations, which cause the bond-stretching displacement. Therefore, we take into account four stretching mode of C—F bonds: Q_1, Q_2, Q_3, and Q_4. In T_d symmetry, these vibrational modes are classified into two irreducible representations, a symmetric mode A_1 (denoted as Q_a) and threefold-degenerate asymmetric modes T_2 (denoted as Q_x, Q_y, and Q_z),

$$Q_a = \frac{1}{4}(Q_1 + Q_2 + Q_3 + Q_4),$$

$$Q_x = \frac{1}{4}(-Q_1 + Q_2 - Q_3 - Q_4),$$

$$Q_y = \frac{1}{4}(-Q_1 + Q_2 + Q_3 - Q_4),$$

$$Q_z = \frac{1}{4}(Q_1 - Q_2 + Q_3 - Q_4). \tag{1}$$

The A_1 mode preserves the T_d symmetry of the molecule, while the T_2 mode causes the atomic displacement which makes the symmetry change from T_d to C_{3v}. On the other hand, the Rydberg states are considered to be coupled with the breathing mode only weakly because of their diffused wave functions.

The Hamiltonian in the core excited state is given by

$$H = E_{a_1}|a_1\rangle\langle a_1| + \sum_{i=x,y,z} E_{t_2}|t_{2i}\rangle\langle t_{2i}| + \sum_{i=x,y,z} E_R|p_i\rangle\langle p_i|$$

$$+ C \sum_{i=x,y,z} (|t_{2i}\rangle\langle p_i| + \text{H.c.}) + A \sum_{i=x,y,z} Q_i(|a_1\rangle$$

$$\times \langle t_{2i}| + \text{H.c.}) + B(Q_x|t_{2y}\rangle\langle t_{2z}| + Q_y|t_{2z}\rangle$$

$$\times \langle t_{2x}| + Q_z|t_{2x}\rangle\langle t_{2y}| + \text{H.c.}) + D_1 Q_a \Big(|a_1\rangle\langle a_1|$$

$$+ \sum_{i=x,y,z} |t_{2i}\rangle\langle t_{2i}| \Big) + D_2 Q_a \sum_{i=x,y,z} |p_i\rangle\langle p_i| + \hbar\omega_{A_1} a^\dagger a$$

$$+ \sum_{i=x,y,z} \hbar\omega_{T_2} b_i^\dagger b_i \tag{2}$$

with

$$Q_i = \frac{1}{\sqrt{2}}(b_i^\dagger + b_i), \qquad i = x,y,z, \tag{3}$$

$$Q_a = \frac{1}{\sqrt{2}}(a^\dagger + a). \tag{4}$$

In the above equation, E_{a_1}, E_{t_2}, and E_R are energies of $|a_1\rangle$, $|t_{2i}\rangle$, and $|p_i\rangle$, b_i is the annihilation operator for the asymmetric vibration mode T_2 with energy $\hbar\omega_{T_2}$, and a is the annihilation operator for the symmetric mode A_1 with energy $\hbar\omega_{A_1}$. The parameter A represents the coupling constant of the quasi-Jahn-Teller interaction between $|a_1\rangle$ and $|t_2\rangle$, and B represents that for the Jahn-Teller interaction. It should be noted that the T_2 mode induces the Jahn-Teller interaction and the quasi-Jahn-Teller interaction simultaneously because of the absence of inversion symmetry in the CF_4 molecule. The vibronic interaction between the symmetric mode and the antibonding molecular orbitals and the Rydberg states is denoted as D_1 and D_2, respectively. We assume a hybridization between the Rydberg states and the molecular orbitals in the core excited state. The off-diagonal coupling between these states is denoted as C.

Since the energies of the vibrational quanta are fairly large (~ 0.1 eV), we can safely assume that the molecule is in its ground state of the vibrational modes in the initial state. The absorption spectrum $F(\Omega)$ for the x ray with energy Ω is calculated by Fermi's golden rule,

$$F(\Omega) = \sum_k \sum_{i=x,y,z} |\langle\Psi_k|\hat{P}^i|\Psi_g\rangle|^2 \delta(\Omega - E_k + E_g). \tag{5}$$

In the above equation, $\hat{P}^i$ is the dipole moment operator, $|\Psi_k\rangle$ and E_k are the kth eigenvector and eigenvalue of H, E_g is the energy of the 1s state of C, and $|\Psi_g\rangle$ is the ground-state wave function, which is given by the direct product of the C 1s wave function and the vacuum state of the vibrational quanta. We considered transitions to the antibonding states and Rydberg states. Therefore, $\hat{P}^i$ is given by, aside from irrelevant factors,

$$\hat{P}^i = (\sqrt{1-\beta^2}|T_{2i}\rangle + \beta|R_i\rangle)\langle\phi_{1s}| + (\text{H.c.}), \tag{6}$$

where $|\phi_{1s}\rangle$ is the C 1s state and β is the ratio of transition amplitude to Rydberg state to that to the antibonding state from the core state. The Hamiltonian (1) is diagonalized by expanding $|\Psi_k\rangle$ in a series of basis vectors given by direct products of the electronic states and the number states of the molecular vibrations. Since the vibronic coupling in the excited state is quite strong, the number of basis vectors needed to guarantee convergence becomes fairly large, typically of order of 5×10^6. Actual calculation has been done by using the Lanczos algorithm.

III. RESULTS AND DISCUSSION

The absorption spectrum $F(\Omega)$ has been calculated for various values of parameters. In Fig. 3, a result of calculation is shown. The experimental result [3] is also shown in the inset of Fig. 3 for comparison. The parameter values are chosen as $E_{a_1} - E_g = 298.72$ eV, $E_{t_2} - E_g = 298.67$ eV, $E_R - E_g = 299.54$ eV, $A = 0.24$ eV, $B = 0.80$ eV, $C = 0.11$ eV, $D_1 = 0.19$ eV, $D_2 = 0.10$ eV, and $\beta = 0.07$. The ener-
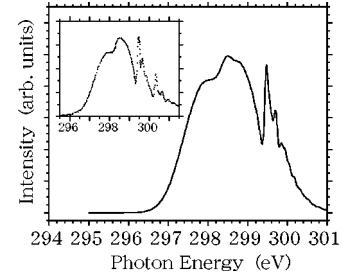

FIG. 3. The calculated C 1s absorption spectrum of the CF_4 molecule. The parameter values are taken so as to reproduce the experimental results (shown in the inset) well.

gies of vibrational quanta are chosen as $\hbar\omega_{T_2} = 0.16$ eV and $\hbar\omega_{A_1} = 0.12$ eV, which is consistent with the experimental data [11]. The continuous spectrum is obtained by assuming a Lorentzian broadening width of the order of 50 meV for each discrete transition line. As shown in Fig. 3, for a suitable choice of parameter values, the calculated result reproduces the experimental line shape very well except for the energy region of transition lines associated with d-like Rydberg states, which is not being considered here. Although the number of parameters to be determined is fairly large, the optimum values are fixed within a relatively small range. Specifically, it has been found that, in order to reproduce the overall features of the main band, it is essential to assume the quasi-Jahn-Teller coupling between the a_1 state and t_2 state as shown below. The molecular orbital calculations of the energy levels of CF_4 have given controversial results about the relative energy positions of a_1 and t_2 [12]. From our theoretical analysis of the line shape, we conclude that the a_1 state lies slightly above the t_2 state in the core excited state.

First we investigate the origin of the structure in the main band, neglecting the Rydberg transitions. This spectrum is denoted as $F_0(\Omega)$. In Fig. 4, we compare theoretical results of the line shape $F_0(\Omega)$ calculated under three different levels of approximations. In Fig. 4(a), the absorption spectrum calculated by the semiclassical approximation for the Jahn-Teller system is shown, where the quasi-Jahn-Teller coupling between the a_1 and t_2 states is neglected. The transition to the Rydberg state is also neglected. The parameter values of B and D_2 are the same as used in Fig. 3. This result is essentially the same as that given by Toyozawa and Inoue [13] in the analysis of the absorption spectrum of the $t_2 \times T_2$ system, which corresponds to the Tl^+-centers in alkali-metal halides. According to them, the absorption spectrum has a logarithmic singularity at the energy of the t_2 state and a pair of side wings located symmetrically in the lower- and higher-energy side of this central peak. It is seen from Fig. 4(a) that the calculated result under the above assumption cannot explain the experimental result, even though the lower-energy side of the main band resembles the experimental data.

In order to investigate the quantum-mechanical effect of the vibration, we have calculated the absorption spectrum again for the same model as in Fig. 4(a), not by the semiclassical approximation but by an entirely quantum-mechanical treatment. The calculated spectrum is shown in Fig. 4(b). The intensity of the higher-energy side is reduced and the spectral shape becomes asymmetric as compared
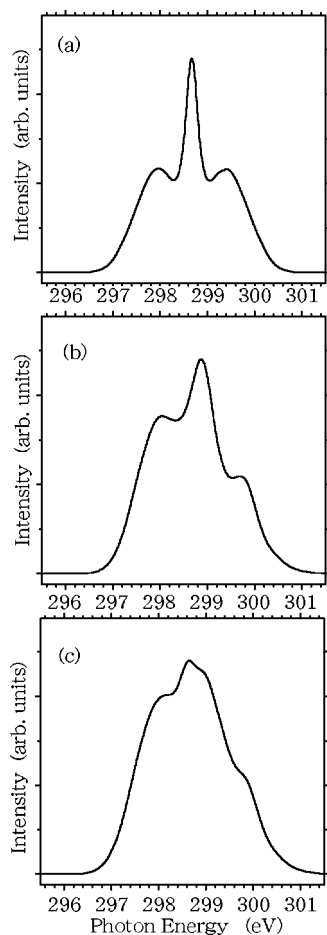
FIG. 4. The C $1s$ absorption spectra of the CF_4 molecule by semiclassical calculation (a), and the quantum-mechanical calculation for the Jahn-Teller system (b) without the quasi-Jahn-Teller coupling. (c) is the result of the quantum-mechanical calculation in which both the Jahn-Teller and quasi-Jahn-Teller couplings are considered. The transition to the Rydberg state is neglected for simplicity.

FIG. 5. The cross-sectional view of the adiabatic potential surfaces in the core excited state along one of the C—F bond axes (Q_1). The branches for the e state and two a_1 states in C_{3v} symmetry are drawn by the solid and broken lines, respectively. The overall feature of the potential surfaces is shown in (a). In (b), the potential surfaces are displayed in an enlarged scale.

with the semiclassical calculation. This is a general tendency of the quantum-mechanical effect of vibronic couplings [14,15]. It should be noted that, although the agreement with the experimental data becomes improved, there still remains a discrepancy: The calculated central peak is too sharp and has too much intensity as compared with the experimental one.

Finally, we consider the quasi-Jahn-Teller coupling between the a_1 and t_2 states in addition to the Jahn-Teller coupling. The result of the quantum-mechanical calculation is shown in Fig. 4(c). It is found that the agreement with the experimental data becomes satisfactory except for the Rydberg transition lines, which are not considered here. This analysis confirms that the main band of the absorption spectrum of CF_4 is attributed to the transition to the unoccupied valence orbitals strongly coupled with molecular deformation. From comparison of Fig. 3 and Fig. 4, it is concluded that not only the Jahn-Teller coupling for the t_2 states but also the quasi-Jahn-Teller coupling between the a_1 and t_2 states is important in determining the line shape of the main band. It is found that the spectral shape around the central peak is sensitive to the choice of the quasi-Jahn-Teller cou-
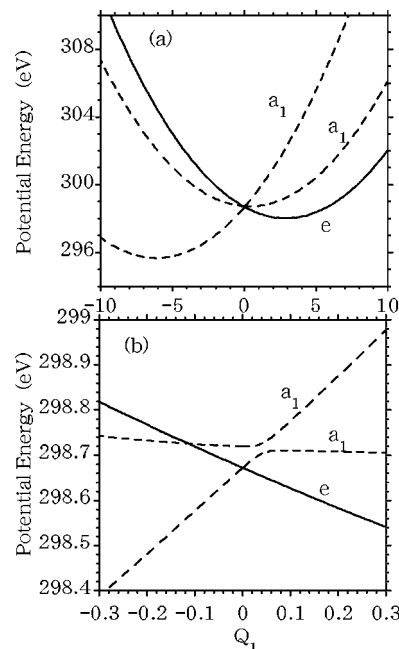
pling constant as well as to the relative energy position of the a_1 and t_2 states. In our analysis, the t_2 state is estimated to be lying 50 meV lower than the a_1 state.

It is instructive to see the calculated adiabatic potentials in the core excited state for the parameter values used in Fig. 3. The cross-sectional view of the adiabatic potential surfaces along one of the C—F bond axes (chosen as Q_1) is shown in Fig. 5(a), where the negative direction corresponds to the elongation of the C—F bond. The adiabatic potentials for the Rydberg states lie far above in this energy scale. The t_2 states lie 50 meV lower than the a_1 state at $Q_1=0$. For $Q_1 \neq 0$, the molecular symmetry is lowered to C_{3v} from T_d, and the t_2 states split into a_1 and e irreducible representations of the C_{3v} point group.

The potential surfaces along Q_1 for two a_1 states in C_{3v} symmetry, one originating from the $4t_2$ states and the other from the $3a_1$ state, are strongly mixed with each other and show an avoided crossing due to the quasi-Jahn-Teller coupling as displayed in Fig. 5(b) in an enlarged scale. This suggests that the resonant excitation of the C $1s$ electron to the molecular orbitals in CF_4 will trigger a bond-breaking molecular deformation. Furthermore, it should be noted that the adiabatic potential surfaces are so close to each other near $Q_1=0$ that the nonadiabatic effect becomes important in the absorption process. This indicates that, in order to reproduce the actual line shape of the absorption spectrum, one must treat the vibronic interactions not semiclassically but entirely quantum mechanically, as has been shown in Fig. 4.

Next, we investigate the Rydberg transition lines. In contrast to the molecular orbitals, the Rydberg states are spatially extended and are essentially of nonbonding character,
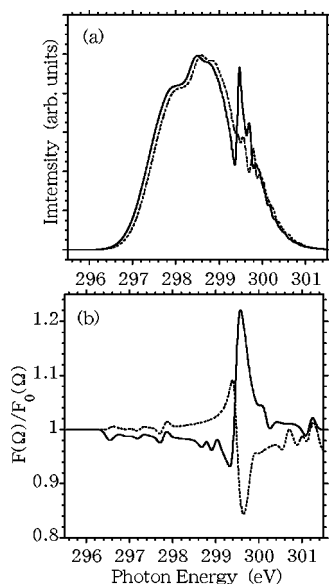
FIG. 6. The calculated absorption spectra $F(\Omega)$ for positive value (solid line) and negative value (dotted line) of β with a fixed value of $|\beta|$ (a). The total absorption intensity normalized by that for the spectrum in which the Rydberg transition is neglected is shown in (b).

so that the vibronic couplings for these states are considered to be weak. This is seen by the comparison of the overall spectral features of C $1s$ absorption in CF_4 and CH_4 molecules [3]. In CF_4, vibrational side bands for the breathing mode are clearly seen in addition to the sharp fundamental Rydberg transition lines at 299.5 eV and at 300.3 eV. The experimental line shape is well reproduced by our calculation.

The most remarkable feature of the Rydberg transition is the existence of a sharp dip in the lower-energy side of the fundamental absorption line. This structure reminds us of the Fano effect [16] in the absorption spectra due to the interference between discrete autoionized states and ionized continua. It should be noted, however, that the dip structure appears sufficiently below the ionization threshold. In this case, the valence orbital states broadened by the vibronic couplings take the place of the electronic continuum in the usual case. The interference between the transitions to the valence orbital states and to the Rydberg states occurs because of the configuration interaction in the excited states. Such a *vibronic* Fano effect has been observed in large aromatic molecules and called Rydberg antiresonance [17,18]. This type of antiresonance structure has also been found in solids [19]. There are several theoretical works on the Rydberg antiresonance [18,20], most of which adopt the semiclassical approximation. In the present work, the densely distributed vibronic states serve as a quasicontinuum and the interference effect is automatically incorporated in the numerical solution of the vibronic problem.

It has been found that the line shape around the Rydberg transition is sensitive to the mixing strength C. It is estimated that $C = 0.11$ eV from the fitting of the experimental data. The line shape is also sensitive to the relative sign of the transition amplitudes to the Rydberg state and the valence states, as it should be. In Fig. 6(a), we compare the calcu-

lated absorption spectra for a positive value (solid line) and a negative value (dotted line) of β with a fixed value of $|\beta|$. In order to see the interference effect more clearly, we show in Fig. 6(b) the ratio $F(\Omega)/F_0(\Omega)$, namely the total absorption intensity normalized by that for the spectrum in which the Rydberg transition is neglected, with the sign of β as a parameter. As shown here, the position of the antiresonance dip changes as the sign of β is reversed. To be more precise, it depends on the relative sign of C and β, and from this analysis we conclude that $C\beta > 0$.

IV. CONCLUDING REMARKS

In this work, we have theoretically investigated the C $1s$ absorption spectrum of the CF_4 molecule by a vibronic model, in which the Jahn-Teller coupling within the t_2 states, the quasi-Jahn-Teller coupling between the a_1 and the t_2 states, and the mixing between the Rydberg states and the valence states are taken into account. The absorption spectrum is calculated rigorously by numerical diagonalization of the vibronic Hamiltonian. For an appropriate choice of parameter values, a good agreement between the calculated and observed spectra is obtained.

The main band with a broad width is attributed to the transition to the valence orbitals, and the sharp lines are attributed to the Rydberg transition lines with their vibrational side bands. It is found that the quasi-Jahn-Teller coupling between the a_1 and t_2 states plays an essential role in determining the line shape of the main band, and the quantum-mechanical effect of the vibronic coupling is important. As a result of the interaction between the energetically broadened valence orbitals and the Rydberg states, the interference between the transitions to both states causes the Rydberg antiresonance.

As can be seen from Fig. 5, the T_d-symmetric configuration of the CF_4 molecule is no longer stable in the core excited state. When the core electron is excited resonantly to the valence orbitals, one of the C—F bonds is elongated and the excited electron is localized to this bond, reducing the symmetry from T_d to C_{3v}. A similar situation has been encountered in the case of lattice deformation in the C $1s$ core-exciton state in diamond [21]. As has been discussed in detail in a previous paper [21], whether the conformational deformation from T_d to C_{3v} symmetry occurs or not depends on the competition between the energy gains by the localization and the delocalization of the excited electron. Namely, the symmetry breaking deformation occurs when the vibronic relaxation energy overcomes the energy gain due to the transfer effect of the electron over four equivalent antibonding orbitals. A *phase diagram* for the stable configuration has been derived in the parameter space (ϵ, A, B), where $\epsilon = E_{t_2} - E_{a_1}$. In the present case, however, the T_d-symmetric configuration is always unstable since $\epsilon < 0$ [13,21].

The study of molecular dissociation under core excitation has been a very active field of research in recent years [9,22]. It has recently been revealed that, in some molecules, the nuclear motion leading to molecular dissociation occurs within the lifetime of Auger decay of core holes [8,9], in contrast to the conventional idea that the Auger decay always precedes the dissociation. It is expected from Fig. 5 that such an ultrafast nuclear motion in the core excited state occurs

also in CF_4. In fact, Neeb *et al.* [6] and Ueda *et al.* [23] have experimentally verified, by resonant Auger electron and photoion coincidence measurement, that a certain dissociation mode is enhanced by resonant excitation of the C $1s$ electron to the valence orbitals in CF_4. The theoretical analysis of molecular dissociation dynamics of CF_4 under resonant x-ray excitation based upon the vibronic model is now proceeding and will be published elsewhere.

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