Vibrational effects in the shape resonant photoionization leading to the A^2T_{1u} state of SF_6^+

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The Chase's adiabatic approximation and Schwinger variational technique in static-exchange approximation are applied to investigate the effect of vibrational averaging on the shape resonant photoionization leading to the A^2T_{1u} state of SF_6^+ . For this study, two of the S-F stretching vibrations are considered: the ν_1 symmetric stretching mode and the two degenerate ν_2 asymmetric stretching modes. Present work concludes that averaging over the asymmetric stretching mode of vibration reduces the peak e_g resonant cross section by 45% relative to the results obtained at the equilibrium nuclear configuration, which agrees with experimental observation. However, the e_g shape resonance is not affected significantly by averaging over the ν_1 symmetric stretching mode of vibration.

Keywords: Photoionization, Shape resonance, Symmetric stretching, Asymmetric stretching

I. INTRODUCTION

Owing to the significance of shape resonances in the photoionization process, sulphur hexafluoride has been the subject of many important studies in physics and chemistry for few decades [1-12]. Photoionization dynamics of valence and core subshells of SF_6 is significantly affected by the shape resonances, occurring both below and above the ionization threshold. The origin of these anomalous resonances was earlier thought to be due to an electrostatic barrier in the molecular potential, created by the surrounding electronegative atoms [1,6,8,13,14]. The virtual valence orbitals located within the potential barrier would then cause enhanced intervalence shape resonant transitions. In contrast to this explanation, later studies revealed that these peaks are due to the shape resonant transitions, caused by the pseudo-bound states trapped in high angular momentum barriers [12].

Trapping of electrons in the angular momentum barrier leading to shape resonance is essentially a single particle process, thus described well by the one-

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electron approximations. However, the shape resonances in the photoionization spectra can couple several outgoing electron channels, leading to significant changes in photoionization dynamics. Therefore a more accurate study of shape resonance requires inclusion of many-electron correlation effects [4,11]. Similarly, shape resonances can induce coupling between electronic motion and vibrational motion, causing the photoionization parameters to be sensitive to molecular geometry near a shape resonance [15,16]. Such photoelectron-vibrational coupling is manifested as considerable deviations from the Franck-Condon vibrational intensity distribution.

There have been number of experimental and theoretical studies aimed at understanding the coupling between electronic and vibrational transitions. Some of the major works include, investigation of non-Franck-Condon effects in the photoionization spectrum of CO[16,17] and O₂[18], studies of vibrational effects on photoionization of CO₂[15,19,20], N₂O[21], CS₂[22], SiF₄[23] etc. Mostly, computational studies on vibrationally resolved photoionization employed adiabatic approximation, which in the context of electron-molecule scattering is known as the Chase approximation [24]. However, such photoionization studies on larger polyatomic systems have been very few in the literature. In the present work we examined the vibrational effects in the shape resonant photoionization leading to the A^2T_{1u} state of SF₆⁺.

SF₆ is particularly interesting in the context of vibrational effects on shape resonances because photoionization from the valence and inner subshells are dominated by the presence of series of resonant peaks. There are many theoretical and experimental studies of the effects of shape resonances on the photoionization parameters of SF₆ [1-14]. It has been confirmed from previous results that there are four prominent shape resonances with symmetries a_{1g} , t_{1u} , t_{2g} , and e_g in the photoionization spectra of the valence orbitals of SF₆. Assignment of these resonances was in great dispute because of the ambiguity in ordering of valence orbitals [5,6]. Based on several theoretical and experimental studies, the orbital configuration $4t_{1u}^6 1t_{2g}^6 3e_g^4 (5t_{1u}^6 + 1t_{2u}^6) 1t_{1g}^6$ has been widely accepted, which is the orbital ordering adopted in the present work.

Photoionization from the $5t_{1u}$ subshell is characterized by two narrow shape resonances, which are attributed to the $5t_{1u} \rightarrow t_{2g}$ and $5t_{1u} \rightarrow e_g$ transitions, with respective widths of 1.00 eV and 1.364 eV. The width of a shape resonance is primarily controlled by the component of angular momentum which traps the outgoing electron. Highly symmetric molecules such as SF_6 [5,6] and C_6F_6 [25] can have very sharp resonances because of the high angular momentum barrier caused by components with high l values. For example, one can see from earlier work that the t_{2g} and e_g channels from SF_6 are trapped by the $l=6$ component of angular momentum [12], which makes the shape resonance sharp. Experimental studies show that influence of the e_g resonance on the valence shell photoionization of SF_6 is more pronounced on the asymmetry parameters than in the cross section [1,5]. However, in almost all theoretical investigations, the e_g resonance appears to be quite strong in the cross section profile. A static-exchange (STEX) photoionization cross section has the e_g resonance with peak value of about ~ 50 Mb at photon energy of 38 eV [11], while in the experimental profile it is visible as a small shoulder-like structure with a peak value of 20 Mb. A similar resonance has appeared in all theoretical e- SF_6 scattering calculations [10,12], but is not visible in experiment [26,27]. This disagreement between theory and experiment was earlier thought to be due to the omission of important interchannel coupling effects in the calculations. In contradiction to this belief, recent coupled-channel calculations [4,11] also exhibited the e_g resonance in the photoionization cross section in line with previous theoretical results. In the present work, we address this discrepancy between theory and experiment near the e_g resonance by considering the effects of stretching vibrations.

The vibrational structure of the photoelectron spectrum of SF_6 was experimentally studied using HeII and synchrotron radiations [1,2,8]. It was found that, the normal modes that are strongly excited in SF_6 are the $\nu_1(a_g)$, $\nu_2(e_g)$ and $\nu_5(t_{2g})$ vibrations. For the present study, two of the S-F stretching vibrations are considered, the ν_1 symmetric stretching mode and the doubly degenerate ν_2 asymmetric stretching mode. We investigate the effects of these modes on the e_g

shape resonance. Vibrational averaging of fixed-nuclei cross sections is done employing the adiabatic Chase approximation. In this approximation, the electronic transition matrix elements are computed at a series of fixed nuclei geometry corresponding to normal mode of vibration. The vibrationally resolved transition amplitudes are obtained by performing an integral of the transition matrix element with appropriate vibrational wavefunctions over the different geometries. The present work concludes that averaging over the ν_2 asymmetric stretching mode reduces the peak e_g resonant cross section by 45% relative to the results obtained at the equilibrium nuclear configuration. This reduction in the peak magnitude of the cross section partly explains why the e_g resonance is not pronounced in the experimental spectrum.

The paper is organized as follows: Section II briefly discusses the theoretical methods employed, Section III gives the computational details, results are examined in Section IV, and conclusions are given in Section V.

II. THEORETICAL METHOD

The calculation of vibrational averaged cross sections is performed invoking Chase's adiabatic approximation [24]. This approximation has been successfully applied in the case of several linear and non-linear molecular systems to understand coupling of vibrational motion with the photoionization process. In Chase's adiabatic approximation, photoionization cross sections are computed at a series of fixed molecular geometries. Vibrational specific cross sections are then calculated by performing an integral over the geometry with the appropriate vibrational wave functions for the initial-neutral and final-ion molecular states.

In the adiabatic approximation, the molecular wave function is assumed to depend on the set of nuclear coordinates q , therefore the initial molecular state is represented as

$$\Psi_i(r; q) = \psi_i(r; q) \varphi_{i,\nu}(q), \quad (1)$$

where r represents all electronic coordinates and $\varphi_{i,\nu}(q)$ is the initial vibrational wave function with quantum number ν , described here by independent harmonic

oscillators for each normal mode. Similarly, the final state molecular wave function is written as

$$\Psi_f^-(r; q) = \psi_f^-(r; q) \phi_{f, \nu^+}(q), \quad (2)$$

where $\phi_{f, \nu^+}(q)$ is the final state vibrational wave function characterized by the quantum number ν^+ . The spin and spatial symmetry adapted state function $\psi_f^-(r; q)$ is formed by the product of an N electron Slater determinant corresponding to the target state function and the one electron continuum state function computed at a fixed nuclear geometry described by the variable q .

The fixed-nuclei photoionization amplitude $T_{\vec{k}}^-(\omega, q)$ is obtained employing the Schwinger variational method in the static-exchange (STEX) approximation using ePolyscat set of codes [28,29]. The vibrational specific transition amplitude $A_{\nu \nu^+ \vec{k}}(\omega)$ corresponds to a photoionization process where an electron with

asymptotic momentum $\vec{k}$ and an ion in the vibrational state ν^+ are produced from a molecule in the ground vibrational state ν as a result of interaction with electromagnetic radiation. The transition amplitude $A_{\nu \nu^+ \vec{k}}(\omega)$ is obtained by integrating the product of the initial $\phi_{i, \nu}(q)$, final $\phi_{f, \nu^+}(q)$ vibrational wave functions, and the electronic transition matrix element $T_{\vec{k}}^-(\omega, q)$ over the set of normal coordinates q :

$$A_{\nu \nu^+ \vec{k}}(\omega) = \int_{-\infty}^{\infty} \phi_{i, \nu}^*(q) T_{\vec{k}}^-(\omega, q) \phi_{f, \nu^+}(q) dq. \quad (3)$$

The total vibrationally specific photoionization cross section is obtained by averaging the transition amplitude $A_{\nu \nu^+ \vec{k}}(\omega)$ over all photoelectron and light polarization directions. If only the ground vibrational state is initially populated, the vibrationally averaged cross section is obtained as:

$$I_{\nu \vec{k}}(\omega) = \int_{-\infty}^{\infty} \phi_{i, \nu}^*(q) |T_{\vec{k}}^-(\omega, q)|^2 \phi_{i, \nu}(q) dq. \quad (4)$$

When all the final vibrational states are considered, the closure relation gives the vibrationally averaged cross section in terms of the vibrationally specific transition amplitudes as [30]:

$$I_{\nu\bar{k}}(\omega) = \sum_{\nu'} |A_{\nu\nu'\bar{k}}|^2. \quad (5)$$

In our computed results, we use Eq. (5) to compute the vibrationally averaged cross sections.

Besides the vibrational averaging calculation, a search for resonant state wave functions is also performed using the energy dependent adiabatic static model-exchange (ASME) potential [12]. Success of this method was earlier demonstrated in the case of one-electron resonances in photoionization and electron scattering. In this approach, the resonance energy is identified by locating poles of the S matrix near the real axis in the complex energy plane. Once the singularities of the S matrix are identified, the actual resonant state wave function can be calculated. Usually, the properties of the resonances found by the ASME potential is comparable to the width and location of them obtained in the STEX approximation. Therefore this method can justifiably be used to interpret the resonance found in the STEX calculation. The ASME states computed using a fixed maximum radius are known as Siegert states with a cutoff potential [31].

III. COMPUTATIONAL DETAILS

The initial molecular state $\psi_i(r;q)$ of SF_6 is computed in a 6-311G(2d,2p) basis set, using GAUSSIAN09 set of codes [32]. The self-consistent field energy of SF_6 in the ground state is -994.219726 hartree. The equilibrium structure of SF_6 has octahedral (O_h) point group symmetry, with S-F bond length $R(\text{S-F})$ as 1.561Å. For the vibrational averaging analysis of SF_6 , we have included three stretching vibrations: the $\nu_1(a_{1g})$ symmetric stretching mode and the doubly degenerate $\nu_2(e_g)$ asymmetric stretching mode. For the calculation of the ν_1 stretching mode, a set of photoionization matrix elements $T_k^-(\omega, q)$ was computed on a grid of seven

evenly spaced normal mode coordinates q , ranging from -3 to 3 where $q = \pm 1$ corresponds to the classical turning points in the ground vibrational state. This corresponds to symmetric oscillation of all S-F bonds around the equilibrium with $R(\text{S-F})$ changing from 1.618 Å to 1.502 Å. The frequencies used to construct the harmonic oscillator vibrational wave functions for vibrational averaging over the ν_1 mode are 774 cm^{-1} for the ground state and 557 cm^{-1} for the excited state [8]. In a similar way, for the degenerate ν_2 stretching mode of vibration the fixed-nuclei matrix elements were calculated on a two-dimensional grid with normal mode coordinates (q_1, q_2) ranging from (-3,-3) to (3,3). In each direction, eight normal mode coordinates were included which were -3, -2, -1, -0.5, 0.5, 1, 2, 3, which represents an asymmetric vibration of S-F bonds around equilibrium, leading to a total of 64 points computed. In this asymmetric mode of vibration, variation of S-F bond lengths from 1.437 Å to 1.685 Å is considered. Note that all these (q_1, q_2) structures retained a D_{2h} symmetry. The molecular vibrational frequencies ν_2 of the initial and excited states we used are respectively 661 cm^{-1} and 588 cm^{-1} .

In this work, vibrational specific photoionization from the $5t_{1u}$ subshell is considered. The fixed-nuclei ionization potential varies slightly as the geometry changes. Since the adiabatic theory neglects the energy shifts of the perturbed target states [24], the present set of calculations employs the equilibrium ionization potential of the $5t_{1u}$ subshell, which is 16.9 eV, as the threshold for all geometries [5]. The valence configuration: $4t_{1u}^6 1t_{2g}^6 3e_g^4 (5t_{1u}^6 + 1t_{2u}^6) 1t_{1g}^6$, is adopted for comparing theoretical and experimental results.

IV. RESULTS AND DISCUSSION

Photoionization from the HOMO-1 ($5t_{1u}$) and the HOMO-2 ($1t_{2u}$) subshells of SF_6 are particularly interesting because of the series of resonances exhibited in their photoionization cross sections. These subshells, being nearly degenerate, are considered together ($5t_{1u} + 1t_{2u}$) in all works. The cross section profiles summed over the $5t_{1u}$ and $1t_{2u}$ orbitals exhibit two shape resonances, having t_{2g} and e_g symmetries. In Fig. 1, photoionization cross sections from the $5t_{1u} + 1t_{2u}$ orbitals

obtained in experimental [1,7] and several theoretical studies [4,7,11] are compared, particularly in the region of e_g resonance. The complex-Kohn (CKohn) and the Time dependent density functional theory (TDDFT) include interchannel coupling correlation effects compared to STEX, Kohn-Sham (KS), and MS-X α calculations which are computed in one-electron approximations. As can be seen in Fig. 1, all theoretical results exhibit the same quantitative trend, which is to overestimate the peak of the e_g resonant cross section. This comparison, therefore, motivated the present study to consider vibrational effects in the theoretical calculations since all previous calculations were performed using fixed nuclei. In the present study, vibrational averaging of the $5t_{1u}$ subshell cross section alone is considered, since the resonance at ~ 35 eV is primarily attributed to the $5t_{1u} \rightarrow e_g$ transition.

FIG 1. Photoionization cross section for the $(5t_{1u}+1t_{2u})$ subshell. Experimental data from Ref. 1 and Ref. 7 are compared with theoretical results: STEX (Present calculation), TDDFT, and KS from Ref. 4, MS-X α from Ref. 7, and CKohn from Ref. 11.

In Fig. 2, we present fixed-nuclei photoionization cross sections for the $5t_{1u}$ subshell leading to the A^2T_{1u} state of SF_6^+ . These STEX cross sections are computed along the symmetric vibrational ν_1 coordinate q to perform vibrational average. The ν_1 normal coordinate q is taken to be negative for geometries with S-F bonds stretched compared to equilibrium. We can see that the e_g resonance is very

sensitive to symmetric nuclear displacement, coupling the ν_1 vibration to the photoelectron dynamics. At larger S-F bond lengths, the resonance moves to lower energy, and at shorter bond length to higher energy. This trend is quite common to molecular shape resonances and can be explained qualitatively using a particle-in-a-box model [23, 25]. Although the position of resonance is sensitive to the symmetric stretch of S-F bonds, the nuclear motion does not affect its shape.

FIG 2. Fixed-nuclei cross section for the $5t_{1u}$ subshell as a function of symmetric geometry.

In Fig. 3, vibrationally averaged and fixed-nuclei $5t_{1u}$ cross sections are compared with experimental result. The fixed-nuclei cross section is calculated at equilibrium geometry ($q=0$) in the STEX approximation. The experimental result corresponds to total photoionization from the $5t_{1u}+1t_{2u}$ subshells, where we have subtracted a constant background to correct for the $1t_{2u}$ cross section which is missing from the calculation. This is justifiable because the region of resonance is dominated by the $5t_{1u} \rightarrow e_g$ transition. The effect of vibrational averaging over the symmetric stretch is to broaden the resonant feature and to reduce the peak cross section by 15%. The resulting vibrationally averaged spectrum overestimates the

peak value at the e_g resonant cross section, indicating that the symmetric stretching vibrations cannot be the source of disagreement between experiment and theory on the apparent strength of the e_g resonance. Although the symmetric bond stretching gives a large energy shift of the resonance, this is not reflected in the vibrationally averaged cross section. Similar behavior is noted in the case of N_2 ; even though there is large deviation of the partial cross section at different fixed internuclear distances, the averaged calculation is only slightly changed[30].

FIG 3: Fixed-nuclei and vibrationally averaged photoionization cross section for the $5t_{1u}$ subshell compared with experimental data [1,7]

We now examine the effects of the degenerate $\nu_2(e_g)$ asymmetric stretch vibrations on the $5t_{1u}$ photoionization. For this, we have sampled fixed-nuclei cross sections on a two dimensional grid of normal mode coordinates (q_1, q_2) . These geometries, with D_{2h} symmetry, correspond to stretching of the S-F bonds asymmetrically around the equilibrium. Photoionization from the symmetry broken geometries leaves the target in electronic states with b_{1u} , b_{2u} , and b_{3u} symmetries, as opposed to triply degenerate t_{1u} state when the molecule has a geometry with O_h symmetry.

Fig 4 shows the fixed-nuclei cross sections corresponding to the $5t_{1u}$ subshell along a line of normal mode geometries $(0.5, 0.5)$, $(0.5, 1)$, $(0.5, 2)$, and $(0.5, 3)$ in the region of e_g resonance. The symmetric geometry cross section with normal mode geometry $(0,0)$ is also given for comparison.

FIG 4: Fixed-nuclei cross section for the $5t_{1u}$ subshell as a function of asymmetric geometry.

We see that the narrow shape resonance in the e_g continuum of the equilibrium geometry is suppressed considerably as a result of $\nu_2(e_g)$ stretching. An analysis of the partial cross sections show that the symmetry broken geometries allow two shape resonances in the a_g continuum symmetry, which were the two degenerate components of the e_g resonance in O_h symmetry. These two resonances are pushed away from each other as two S-F bonds are made longer and simultaneously two others are made shorter, causing the original e_g resonance to become broader and to reduce the peak cross section magnitude.

To see more clearly the effects of asymmetric stretching on the resonance, we analyzed the resonant state wave function of the continuum electron. The energy dependent ASME potential is used to find the location and width of the resonant peaks noted in the cross section of the symmetric and asymmetric geometries. Once

the complex energy of resonance is found, the resonant state wave function of the continuum orbital is calculated and plotted.

FIG 5: Three-dimensional images of the two degenerate e_g resonant wave function in the equilibrium geometry.

Fig. 5 shows the two degenerate components of the e_g resonant orbital in the equilibrium geometry $q=(0,0)$ in xy plane. For the continuum orbital, the resonance parameters, position (E_R), and width (Γ), obtained by the ASME potential are $E_R=35.76$ eV and $\Gamma=1.364$ eV. The resonant energy (E_R) is given as the equivalent photon energy. One can notice that E_R and Γ obtained by the ASME calculation are within a few eV of those found by the fixed-nuclei STEX calculation. This resonant state function behaves like a d orbital around the S atom, and like a p orbital around the F atoms, which is in agreement with structure of dipole prepared continuum e_g orbitals [4].

Fig. 6 shows the resonant state wave function in xy plane corresponding to the non-symmetric geometry $q= (0.5,1)$. For the symmetry broken geometry, two of the S-F bonds in the x direction are made shorter, two other bonds in the y direction are made longer, and the $R(\text{S-F})$ is kept close to the equilibrium bond length in the z direction. In the symmetry broken geometry, two shape resonances in the a_g symmetry are predicted. With reference to the position of original e_g resonance, one of the a_g resonance (Resonance 1) is shifted to lower energy (35.24 eV), while the other (Resonance 2) is pushed to higher energy (36.83 eV). In the left panel of Fig 6, a_g resonant state orbital for Resonance 1 is given, while that for Resonance 2 is in

the right panel. We see that the position and shape of continuum state function is very sensitive to changes in the molecular geometry.

FIG. 6: Three-dimensional image of the a_g resonant wave function in the asymmetric geometry. (a) The resonance shifted to lower energy and (b) and that shifted to the higher energy.

A striking feature of the resonance is that the a_g orbital wave function, when the molecular geometry is non-symmetric, is predominantly trapped between two F atoms in one direction. The resonance, which is moved to lower energy, is trapped near the F atoms with longer bond lengths (y axis). Similarly the resonance located at higher energy is trapped near the two F atoms whose bond lengths are made shorter (x axis). This qualitative behavior of the resonances is similar to that exhibited by the e_g resonances in the case of symmetric stretching. From a different perspective, the asymmetric stretching collapses the continuum orbital in one direction, causing the resonance in SF_6 to behave like those in a linear molecule in the plane where S-F bonds are changed. One can also assume that the shape resonance in the equilibrium geometry is a mixture of individual shape resonances, whose amplitudes are on each S-F bonds. When the symmetric geometry is distorted, the degeneracy of these resonances is lifted and they appear as separate shape resonances at different energies.

Table 1 shows the evolution of resonant characteristics E_R , and Γ of two shape resonances obtained by the ASME potential corresponding to a group of geometries with normal mode coordinates $q=(0,0)$, $(0.5, 0.5)$, $(0.5, 1)$, $(0.5, 2)$, $(0.5,$

3) and (3, 3). Positions of the resonant state orbitals tend to move away from each other in response to the asymmetric stretching. When the normal mode coordinate is at (0.5,0.5), the two resonances are located at 35.48 eV and 36.61 eV, while at $q=(3,3)$ they are located at 33.7 eV and 40.15 eV. This behavior is similar to the prediction of the fixed-nuclei STEX calculation, which causes the e_g resonance to become broader. We show in Fig. 7 the positions for the two shape resonances in the asymmetric geometry versus the normal mode coordinates. In the left panel, position of the shape resonance in the lower energy region is given, while that in the higher energy region is in the right panel. It is clear that the two shape resonances move apart from each other, as the geometry is made more non-symmetric. Not only the location, but the width (Γ) of shape resonance is also sensitive to molecular vibrations. From Table 1, one can see that change of Γ is slower in the direction of bond elongation, while faster in the direction of compression of bonds.

Normal mode coordinate q	Resonance 1		Resonance 2	
	E_R (eV)	Γ (eV)	E_R (eV)	Γ (eV)
(0,0)	35.76	1.364	35.76	1.364
(0.5,0.5)	35.48	1.28	36.61	1.42
(0.5,1)	35.24	1.28	36.83	1.44
(0.5,2)	34.66	1.34	38.18	1.64
(0.5,3)	34.25	1.46	39.02	1.76
(3, 3)	33.7	1.49	40.15	2.10

Table 1 Resonant characteristics E_R and Γ of the a_g resonant wavefunctions.

FIG. 7: Positions of the a_g resonant wave functions versus normal mode coordinates. (a) The resonance shifted to lower energy and (b) that shifted to the higher energy.

In Fig. 8 we present the vibrationally averaged $5t_{1u}$ cross section over the $\nu_2(e_g)$ asymmetric stretch vibrations, compared with fixed-nuclei cross section and experimental results. The effect of vibrational averaging on the STEX cross section is to reduce its magnitude by 45% with reference to that from equilibrium geometry calculation. The averaged cross section shows the same qualitative trend as exhibited by the fixed-nuclei cross section in asymmetric geometries. The width of the shape resonance of the averaged calculation is broader due to the presence of two shifted and broadened a_g resonances. Vibrational averaging over the ν_2 vibrations has made the agreement between theory and experiment reasonable, relative to the results in the equilibrium geometry fixed-nuclei calculation. Therefore a combined $\nu_1(a_g)$ and $\nu_2(e_g)$ vibrational averaging might account to a total reduction of 60% of cross section compared to the STEX calculation result at equilibrium geometry.

FIG. 8: Fixed-nuclei and vibrationally averaged photoionization cross section for the $5t_{1u}$ subshell compared with experimental data [1,7].

The better agreement between present theoretical results and experiment indicates that the e_g resonance in the experimental cross sections is substantially suppressed by the asymmetric stretching vibrations. The further disagreement between theory and experiment could be generally due to the neglect of vibrational effects of bending motion in the calculation, which would also tend to broaden the resonance features.

V. CONCLUSIONS

The results presented here illustrate vibrational effects on photoionization cross section from the $5t_{1u}$ subshell leading to the A^2T_{1u} state of SF_6^+ . Averaging over the $\nu_1(a_g)$ symmetric vibration resulted in 15% reduction of the peak resonant cross section, while that over the $\nu_2(e_g)$ asymmetric vibration caused 45% reduction. The SF_6 geometry, stretched asymmetrically, has two a_g shape resonances which correspond to the degenerate e_g resonance in equilibrium geometry. These two resonances are further moved apart with asymmetric stretching, which in turn causes the reduction of cross section when averaged. The improved agreement between theory and experiment suggests that the $\nu_2(e_g)$

nuclear vibrations reduces the impact of the e_g resonance on the photoionization cross sections.

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- Vibrational effects on photoionization from the $5t_{1u}$ subshell of SF_6 are studied.
- Averaging over the symmetric vibration led to 5% reduction of the cross section.
- Averaging over the asymmetric vibration caused 45% reduction of the cross section.
- The $\nu_2(e_g)$ vibrations reduce the impact of the e_g resonance on the cross sections.