

ARTICLE

Observation of a New $^2\Sigma$ Excited Electronic State of SF by Resonance-Enhanced Multiphoton Ionization Spectroscopy[†]

Xian-feng Zheng^{a,c}, Ting-ting Wang^a, Chun-yan Li^a, Yang Chen^{a*}, Jing-song Zhang^b

a. Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics University of Science and Technology of China, Hefei 230026, China;

b. Department of Chemistry, University of California at Riverside, Riverside 92521, USA

c. Department of Physics, Anhui Normal University, Wuhu 241000, China

(Dated: Received on July 25, 2007; Accepted on August 8, 2007)

The (2+1) resonance-enhanced multiphoton ionization (REMPI) spectrum of SF has been obtained in the single-photon wavelength region of 307-321 nm. Five vibronic bands were observed and assigned to the two-photon transitions from the ground state to a $^2\Sigma$ Rydberg state. The term value T_e , vibrational frequency, and the rotational constant of the $^2\Sigma$ Rydberg state were determined. Another 2P state was observed near 312 nm.

Key words: SF radical, Resonance-enhanced multiphoton ionization, Spectroscopy

I. INTRODUCTION

The first spectroscopic study of the gaseous radical was carried out by Carrington *et al.* using electron paramagnetic resonance (EPR) spectroscopy [1]. The ground state was confirmed to be $X^2\Pi_i$, and the rotational, spin-orbit interaction, and hyperfine splitting parameters were determined [1]. Later on, more studies of the SF ground state by EPR [2,3], microwave [4,5], and infrared spectroscopy [6] were reported. Infrared spectra of SF in solid argon were obtained by Hassanzadeh and Andrews in 1992 [7]. In 2001, Morino and Yamada measured pure rotational transitions of the SF radical in the ground state $^2\Pi_i$ in millimeter- and submillimeter-wave region and revised some molecular constants [8]. The electronic spectrum of SF was first reported by Lonard and Trombetti in 1970 [9]. In the 330-400 nm region, about 40 absorption bands that were believed to be from the SF radical were observed, which were assigned to be due to the $A^2\Pi \leftarrow X^2\Pi_i$ transition. The excited $A^2\Pi$ state has an electronic origin at $\sim 25060 \text{ cm}^{-1}$ and a spin-orbit splitting of 387 cm^{-1} ; the vibronic bands of SF below 350 nm are diffuse. More recently, a $^2\Delta$ Rydberg state was identified by resonance-enhanced multiphoton ionization (REMPI) spectroscopy in the region of 70300 cm^{-1} [10]. Experimental work on the thermochemistry of SF_n , both ions and neutrals, has been carried by Hildenbrand [11], Fisher *et al.* [12], and Cheung *et al.* [13]. The ground state of SF^+ is $^3\Sigma$ state with the electronic configuration of (core)(7σ)²(2π)⁴(3π)². The adiabatic ionization

energy was experimentally confirmed to be 10.09 eV [11,12].

SF and its electronic states have also been investigated theoretically. The dipole moment, ionization energy ($10.4 \pm 0.4 \text{ eV}$), and electron affinity of the ground state of SF were obtained by O'Hare and Wahl using SCF wavefunctions near the Hartree-Fock limit [14,15]. The R-matrix method was used by Baluja and Tossell to study electron collisions with the SF radical. Six electronic excited states, $^4\Sigma^-$, $^2\Sigma^-$, $^2\Delta$, $^2\Sigma^+$, $^2\Pi$, and $^4\Pi$, were predicted to have vertical excitation energies in the range of 3.32 - 9.48 eV , with the $^2\Sigma^+$ state calculated to be $\sim 61300 \text{ cm}^{-1}$ [16]. More recently, the ground and valence-excited states of SF were examined using multireference configuration interaction with single and double excitations+Q study [17]. The potential energy curves of several low-lying electronic excited states were calculated; the $^4\Sigma^-$, $^2\Sigma^-$, and $^2\Delta$ states were bound, while $^2\Sigma^+$, $^2\Pi(\Pi)$, and $^2\Sigma(\Pi)$ were repulsive. The excited state observed in the region of 25060 cm^{-1} by Di Lonard and Trombetti was likely the $^2\Sigma^-$ and $^2\Delta$ state instead of the $A^2\Pi$ state.

The electronic structure and bonding of SF are similar to those of the iso-valence and iso-electron OCl radical, which would be helpful in analyzing and understanding the spectrum of the SF radical. The ground state of SF/OCl is $X^2\Pi$, corresponding to the same valence electronic configuration (7σ)²(2π)⁴(3π)³, the spin-orbit splitting of $X^2\Pi$ for SF is -387 cm^{-1} [1], close to that of OCl (-322 cm^{-1}) [18]. The first excited state of the SF radical reported by Lonard and Trombetti is $A^2\Pi$ with electronic energy $T_e \sim 25000 \text{ cm}^{-1}$ and the spin-orbit splitting $-599 \pm 20 \text{ cm}^{-1}$ [9]. For the OCl radical, the first excited state is $A^2\Pi$ with electronic energy $T_e \sim 26098 \text{ cm}^{-1}$ and the spin-orbit splitting -521 cm^{-1} [19]. The existence of a second valence excited state for OCl, $B^2\Sigma^+$, presumably with the va-

[†]Part of the special issue "Cun-hao Zhang Festschrift".

*Author to whom correspondence should be addressed. E-mail: yangchen@ustc.edu.cn

lence electron configuration $(7\sigma)^1(2\pi)^4(3\pi)^4$, has not been confirmed directly, it is estimated to be located at $\sim 31000\text{ cm}^{-1}$ above the ground state. Another excited state of the OCl radical, $C^2\Sigma^-$, has been confirmed to be a low-lying Rydberg state with the electronic energy $T_e \sim 58490\text{ cm}^{-1}$ [20].

In this study, a new excited electronic state $^2\Sigma$ lying in 62600 cm^{-1} was identified by two-photon resonance-enhanced multiphoton ionization (REMPI) spectroscopy between 306.7 and 320.5 nm. In addition, a $^2\Pi \leftarrow X^2\Pi_i$ transition was observed, and the related spectral constants were derived through the rotational analysis.

II. EXPERIMENTS

The experimental apparatus used in this work was a laser ionization time-of-flight (TOF) mass spectrometer that was described before [10]. It consisted of a pulsed radical generation source, a pulsed Nd:YAG-pumped frequency-doubled dye laser, a TOF mass spectrometer, an microchannel plate (MCP) ion detector, and a computer data acquisition system. SF radicals were generated by pulsed dc discharge of SF₆(10%) seeded in Ar [10]. The gas samples used in this study were of purity of 99.99% for SF₆ and Ar. Two electrodes were electronically isolated by insulators from each other and from the pulsed valve. The discharge took place in the small space between the electrodes, when a high-voltage pulse was applied to one of the electrodes just after the mixed gas was pulsed through the valve. The gas passing and pulsed HV were sequenced by a pulse generator (SRS, DG535) in order to stabilize discharge and to maximize the signal intensity of the SF radicals. The background ions generated from the discharge were effectively eliminated by the deflection electric field of two parallel plates installed between the pulsed discharge nozzle and the skimmer. The applied deflection electric field was up to 200 V/cm in our experiment.

The light source used was a dye laser (Lumonics, HT500) pumped with the second harmonic (532 nm) of a Nd: YAG laser (Spectra-Physics, GCR-250) operating at 10 Hz. The dye laser output was frequency-doubled with a doubler (Lumonics, HT1000). The laser dye R610 was used in this study. The frequency-doubled laser output, with $\sim 0.5\text{ mJ/pulse}$ and $< 0.1\text{ cm}^{-1}$ bandwidth, was focused by a lens ($f=250\text{ mm}$) into the photo-ionization zone. The dye laser wavelength was scanned in an increment of $0.01\text{--}0.0001\text{ nm/s}$. The wavelength of the dye laser was calibrated against the synchronically recorded argon atomic lines corresponding to the transition from the metastable state $4s^2[3/2]_2^o$ or $4s^2[1/2]_0^o$. The ions generated by the REMPI process were detected by the TOF mass spectrometer. The ion signal from mass spectrometer was pre-amplified, fed into a transient digitizer, and averaged with a computer data acquisition system. The

REMPI excitation spectra of SF were obtained through measuring the $^{32}\text{SF}^+$ ion signal as a function of laser wavelength. The presented spectral intensity has not been normalized with the dye laser intensity. The experimental apparatus and method used for the present studies of the free radicals have been proved to be reliable by observing the known rotationally resolved $^2\Delta \leftarrow ^2\Pi$ spectrum of the CCl radical and the atomic spectral lines of Ar Rydberg states.

III. RESULTS AND ANALYSIS

In this study, three typical mass spectra of SF were investigated with the same laser energy and were shown in Fig.1. As shown in Fig.1, the strong $^{32}\text{SF}^+$ ion signal appeared only in Fig.(c) when both the discharge and the REMPI laser radiation were present. No mass peaks of SF_n^+ ($n=2\text{--}6$) were observed, and thus the SF^+ signal should be directly from the multiphoton ionization of neutral SF radicals rather than from the ionization fragmentation products of multiphoton ionization of SF_n ($n=2\text{--}6$). Furthermore, the spectral assignments discussed below strongly support that the excitation spectra originate from the multiphoton ionization of neutral SF radicals.

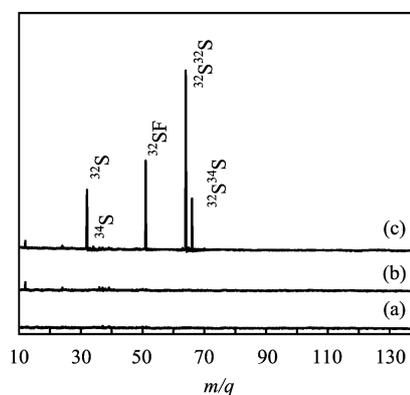


FIG. 1 TOF mass spectra averaged over 256 laser shots: (a) with dc discharge alone, (b) with 311.5 nm laser irradiation alone, and (c) with dc discharge and the 311.5 nm laser irradiation.

Figure 2 shows the REMPI spectrum of the SF radical between one-photon wavelength 306.7 and 320.5 nm. The measurement of the ion signal was carried out on $^{32}\text{SF}^+$ ($m/z=51$). In this wavelength region, five bands are relatively prominent. Four of them, locating at 307.4, 311.4, 315.4, and 319.4 nm, are regularly spaced in energy and have identical band contour, and this group of bands are tentatively assigned as $^2\Sigma \leftarrow X^2\Pi$. Another band locating at 311.5 nm is obviously different in the band structure from the former, and is assigned as a $^2\Pi \leftarrow X^2\Pi$. The upper trace shown in Fig.2 is the REMPI spectrum of metastable argon atom and is used to calibrate the dye laser wavelength.

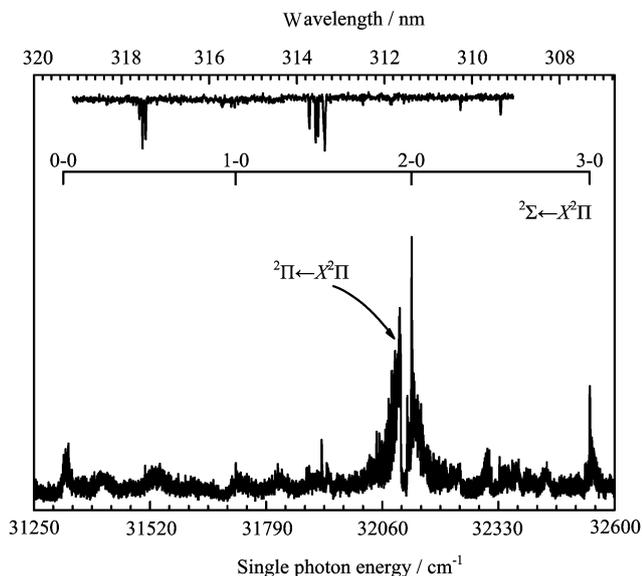


FIG. 2 Experimental REMPI spectra of SF (lower trace) and metastable argon for wavelength calibration (upper trace) with the one-photon energy in the range of 31250–32600 cm^{-1} .

A. ${}^2\Sigma\leftarrow X^2\Pi$

The bands assigned as ${}^2\Sigma\leftarrow X^2\Pi$ have common characters, with violet degraded and two sharp heads appearing in each band, as shown in Fig. 3. Along the progression the average interval between adjacent bands is $\sim 407.5 \text{ cm}^{-1}$. These characters indicate that these bands should belong to one vibrational progression.

Since multiphoton experiment may have more than one possible excitation mechanism, a correct determination of the photon order of the resonant state is critical for assigning the REMPI spectra and for deriving spectroscopic constants. The adiabatic ionization potential IP of the SF radical was measured to 10.09 eV (80973 cm^{-1}) by electron impact ionization mass spectrometry. Therefore, at least three photons of the wavelength between 306.7 and 320.5 nm would be required to ionize the SF radical in the ground state. If observed bands originate from a one-photon resonant excitation, i.e. via the (1+2) REMPI process, the vibrational frequency of the intermediate state would be on the order of 400 cm^{-1} , far smaller than the vibrational frequency (838 cm^{-1}) of the ground state SF [7]. If the electronic transition corresponds to a (2+1) REMPI process, the vibrational frequency of the resonant state is $\sim 815 \text{ cm}^{-1}$, close to the vibrational frequency (828 cm^{-1}) of the ground state of SF^+ . In addition, the quadrate dependence on the laser power was verified in the experiment. Therefore, the observed progression should arise from a two-photon resonance, and the resonance state should be a Rydberg state.

For the Rydberg state, quantum defect can be derived

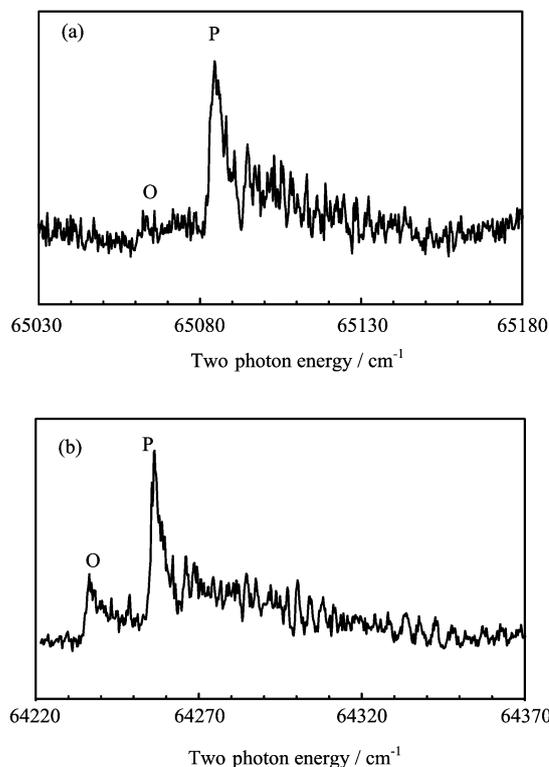


FIG. 3 Expanded region of (a) 307.4 nm band and (b) 311.4 nm band.

by the familiar formula:

$$v_{0-0} = IP_a - \frac{109737}{(n - \delta)^2} \quad (1)$$

where v_{0-0} represents the electronic origin, IP_a is the adiabatic ionization potential in cm^{-1} (for SF, $IP_a = 81390 \text{ cm}^{-1}$), n is the principal quantum number of the centered atom, and δ is the quantum defect. For F atom, the nl ($n \geq 3$) orbital energy ($> 100000 \text{ cm}^{-1}$) is much higher than that of the discussed electronic state, while the 4s, 4p, and 3d orbital energies of S atom range from 55000 cm^{-1} to 70000 cm^{-1} and especially the 4p energy level is close to the band origin ($\sim 62638 \text{ cm}^{-1}$) of the lowest energy band, indicating that the discussed electronic state should be a sulfur-centered Rydberg state. For sulfur-centered Rydberg orbital, the δ values of ns , np , nd , and nf Rydberg states should be around 2.0, 1.6, 0.08, and 0.06, respectively [21]. Quantum defect (δ) may vary only within a limited range for each orbital type. Using the Rydberg formula and the lowest energy band ($\sim 62638 \text{ cm}^{-1}$), one would obtain $n - \delta = 2.413$, which yields three possible sets: ($n=3$, $\delta=0.587$), ($n=4$, $\delta=1.587$), and ($n=5$, $\delta=2.587$). In comparison with the quantum defect for sulfur-centered Rydberg orbitals, the discussed electronic state is likely a 4p Rydberg state.

In order to determine the symmetry of the upper electronic and reasonable assignment of the rotational

branches, the band structure in this band group is compared with that of the $C^2\Sigma^- \leftarrow X^2\Pi$ band of the iso-valence and iso-electron OCl radical [20]. The electronic structure and bonding in SF and in OCl radical are found to be similar. Both SF and OCl have similar band contour, two sharp head with the weaker one appearing in the red of the band, and violet-degraded branch. In addition, the calculation on the electronic states of the SF radical by Baluja *et al.* predicted that a $^2\Sigma$ electronic state with the configuration of $(7\sigma)^2(2\pi)^4(3\pi)^2(7\sigma)$ exists in $\sim 61000 \text{ cm}^{-1}$ [16]. These evidences indicate that the observed band system should arise from the $^2\Sigma^- \leftarrow X^2\Pi$ transition. Taking the scheme of the rotational assignment of OCl radicals adopted by Steege *et al.* [20], the two sharp heads for the band of SF are assigned to be O-branch and P-branch, respectively. The head frequencies of the spectral bands are listed in Table I. The rotational constants can be estimated by the formula,

$$B_v' = \frac{\Delta(\text{OP})B_v''}{\Delta(\text{OP}) - 3B_v''} \quad (2)$$

where $\Delta(\text{OP})$ is the difference of the head frequency of the O- and P-branch. From the constants in Table I, B_v' decreases as expected with the increase of the vibrational quantum v' , and $B_v' > B_v''$, which indicates that the band branch is violet-degraded, consistent with the experimental spectrum. These agreements support that the assignment of $^2\Sigma^- \leftarrow X^2\Pi$ transition is reasonable.

TABLE I Experimental band head positions for SF $^2\Sigma^- \leftarrow X^2\Pi(v''=0)$ transitions (in cm^{-1})

Bands	O branch	P branch	$\Delta(\text{OP})^a$	$B_v'^b$
0-0	62625.0	62638.4	13.4	0.631
1-0	63420.8	63437.8	17.0	0.613
2-0	64236.2	64255.8	19.6	0.604
3-0	65062.6	65084.0	21.4	0.599

^a Calculated with $\Delta(\text{OP})=v(\text{P-branch head})-v(\text{O-branch head})$.

^b Calculated with $B_v'=\Delta(\text{OP})B_0''/(\Delta(\text{OP})-3B_0'')$.

In the present experiment, the SF radicals produced from the dc discharge are dominantly distributed in the $v''=0$ vibrational level of the ground electronic state. Although the focus condition and the laser energy did not vary in the experiment, the density of the SF radicals determined by the dc discharge could not keep constant in the experiments of many days. The spectrum of the isotopic radical ^{34}SF could not be discerned because of the weak intensity. Therefore the upper vibrational assignment could not be given directly from the relative intensity of spectral band and the isotopic shift. However, the vibrational assignment of this progression could be inferred from the quantum defect of this Rydberg state. Three different schemes, which assign the

319.4 nm band as 0-0, 1-0, and 2-0 band, respectively, are applied to calculate the quantum defect with the Rydberg formula. The band origin was approximated with the head frequency of the P-branch and the caused error is estimated to be on the order of 10^{-3} . The quantum defects of 1.59, 1.63, and 1.68 are obtained. The best agreement between the calculated and the expected quantum defect (1.6) for the 4p Rydberg state of the sulfur-centered SF is achieved when assigning the 319.4 nm band as the 0-0 band. Therefore, the vibrational assignments shown in Fig.2 are proposed.

B. 311.5 nm band

Different from the bands of the $^2\Sigma^- \leftarrow X^2\Pi$ transition, the 311.5 nm band appears to be red-degraded, as shown in Fig.4(a). In order to examine the excitation mechanism, the power dependence of the signal was measured. The laser energy was adjusted from 0.4 mJ/pulse to 3.0 mJ/pulse and other experimental conditions were kept unchanged. The logarithm of the ion signal was plotted as a function of logarithm of the detection laser pulse energy (Fig.5). The slope of the linear fit is close to one, which means that it should be a one-photon resonant excitation. Thus, in the experimental wavelength region, the excitation mechanism should be a (1+2) process.

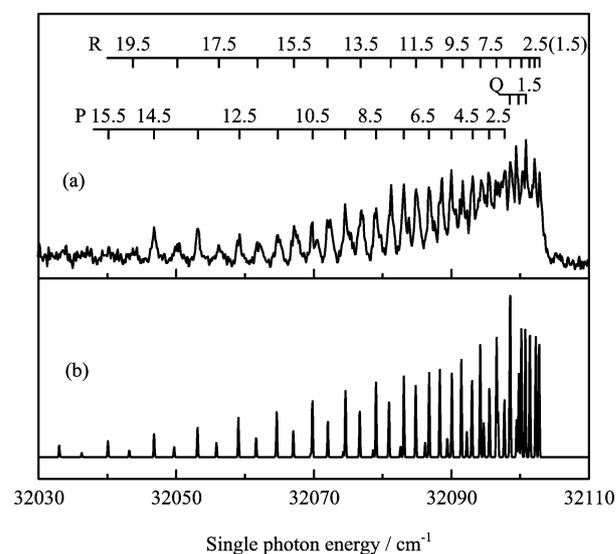


FIG. 4 The 311.5 nm band of SF: (a) experimental spectrum, (b) simulated spectrum.

For the electronic transition from the $^2\Pi$ ground state, the allowed upper states are $^2\Sigma$, $^2\Pi$, and $^2\Delta$. If the studied band belongs to $^2\Sigma^- \leftarrow X^2\Pi$ or $^2\Delta \leftarrow X^2\Pi$, three rotational branches with almost equal intensity are expected. But from the band simulation, this band has a weak Q-branch, and two identical intensity R- and P-branches, and thus it is believed to be a $^2\Pi \leftarrow X^2\Pi$ transition.

The rotational simulation is carried out to determine the rotational constants of the upper and the lower state involved in the transition. For the Π state, it is conventionally described in terms of Hund's case (a) angular momentum coupling scheme. The rotational energy levels could be approximated by

$$E_{\text{rot}} = B_v J(J+1) \quad (3)$$

The Q, P, and R branches can be expressed as

$$Q = T_0 + (B_v' - B_v'')J(J+1) \quad (4)$$

$$P, R(J) = T_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2 \quad (5)$$

where $m = -J$ for the P-branch and $m = J+1$ for the R branch. In the simulation, the line-shape is convoluted with a Lorentzian function and the intensities of the rotational lines are given by the combination of the Hönl-London factor with $S_J^Q = (2J''+1)/[J''(J''+1)]$, $S_J^P = (J''+1)(J''-1)/J''$, and $S_J^R = J''(J''+2)/(J''+1)$, and the Boltzmann distribution with rotational temperature about 40 K. The simulated spectrum is shown in Fig.4. B_v' and B_v'' are derived from the simulation, $B_v' = 0.421 \text{ cm}^{-1}$ and $B_v'' = 0.61 \text{ cm}^{-1}$. The rotational simulation confirms that P-, Q-, and R-branch start from 2.5, 1.5, and 1.5, respectively, which suggests that this band should correspond to a ${}^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition.

IV. CONCLUSION

In this work, a new ${}^2\Sigma$ Rydberg state of SF has been observed via a (2+1) REMPI process in the single-photon excitation wavelength region of 307-321 nm. Rotational analysis of the five vibronic bands of ${}^2\Sigma-X^2\Pi_{3/2}$ transitions has been performed to derive equilibrium rotational constants and vibrational frequency for the resonance excited state. Using the ionization energy of SF with term value for the newly observed ${}^2\Sigma$ state, coupled with quantum defects for the Rydberg state of SF based on those known for atomic sulfur, the ${}^2\Sigma$ state is assigned to the Rydberg state.

V. ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China (No.20328305, No.20433080), and Chinese Academy of Science (KJCX2-SW-H08).

- [1] A. Carrington, G. N. Currie, T. A. Miller, and D. H. Levy, *J. Chem. Phys.* **50**, 2726 (1969).

- [2] C. R. Byfleet, A. Carrington, and D. K. Russell, *Mol. Phys.* **20**, 271 (1971).
- [3] K. Takagi and T. Kojima, *Jpn. J. Appl. Phys.* **13**, 1195 (1974).
- [4] T. Amano and E. Hirota, *J. Mol. Spectrosc.* **45**, 417 (1973).
- [5] Y. Endo, S. Saito, and E. Hirota, *J. Mol. Spectrosc.* **92**, 443 (1982).
- [6] Y. Endo, K. Nagai, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.* **97**, 213 (1983).
- [7] P. Hassanzadeh and L. Andrews, *J. Phys. Chem.* **96**, 79 (1992).
- [8] I. Morino and K. M. T. Yamada, *J. Mol. Spectrosc.* **207**, 10 (2001).
- [9] G. D. Lonardo and A. Trombetti, *Tran. Faraday Soc.* **66**, 2694 (1970).
- [10] T. Wang, X. Zheng, C. Li, and Y. Chen, *Chem. Phys. Lett.* **425**, 185 (2006).
- [11] D. L. Hildenbrand, *J. Phys. Chem.* **77**, 897 (1973).
- [12] E. R. Fisher, B. L. Kickel, and P. B. Armentrout, *J. Chem. Phys.* **97**, 4859 (1992).
- [13] Y. S. Cheung, Y. J. Chen, C. Y. Ng, S. W. Chiu, and W. K. Li, *J. Am. Chem. Soc.* **117**, 9725 (1995).
- [14] P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.* **53**, 2834 (1970).
- [15] P. A. G. O'Hare, *J. Chem. Phys.* **59**, 3842 (1973).
- [16] K. L. Baluja and J. A. Tossell, *J. Phys. B: At. Mol. Opt. Phys.* **36**, 19 (2003).
- [17] X. Yang and J. E. Boggs, *J. Chem. Phys.* **122**, 194307/1 (2005).
- [18] A. G. Maki, F. J. Lovas, and W. B. Olson, *J. Mol. Spectrosc.* **92**, 410 (1982).
- [19] J. A. Coxon, W. E. Jones, and E. G. Skolnik, *Can. J. Phys.* **54**, 1043 (1976).
- [20] D. H. A. ter Steege, M. Smits, C. A. de Lange, N. P. C. Westwood, J. Barrie Peel, and L. Visscher, *Faraday Discussions* **115**, 259 (2000).
- [21] S. T. Manson, *Phys. Rev.* **182**, 97 (1969).