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Satellites of Xe transitions induced by infrared active vibrational modes of CF₄ and C₂F₆ molecules

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Absorption and luminescence excitation spectra of Xe/CF₄ mixtures were studied in the vacuum UV region at high resolution using tunable synchrotron radiation. Pressure-broadened resonance bands and bands associated with dipole-forbidden states of the Xe atom due to collision-induced breakdown of the optical selection rules are reported. The spectra display in addition numerous satellite bands corresponding to transitions to vibrationally excited states of a Xe-CF₄ collisional complex. These satellites are located at energies of Xe atom transition increased by one quantum energy in the IR active ν_3 vibrational mode of CF₄ ($\nu_3 = 1281 \text{ cm}^{-1}$). Satellites of both resonance and dipole-forbidden transitions were observed. Satellites of low lying resonance states are spectrally broad bands closely resembling in shape their parent pressure-broadened resonance bands. In contrast, satellites of dipole-forbidden states and of high lying resonance states are spectrally narrow bands (FWHM $\sim 10 \text{ cm}^{-1}$). The satellites of dipole-forbidden states are orders of magnitude stronger than transitions to their parent states due to collision-induced breakdown of the optical selection rules. These satellites are attributed to a coupling of dipole-forbidden and resonance states induced by the electric field of the transient CF₄ ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) dipole. Similar satellites are present in spectra of Xe/C₂F₆ mixtures where these bands are induced by the IR active ν_{10} mode of C₂F₆. Transitions to vibrationally excited states of Xe-CF₄(C₂F₆) collision pairs were also observed in two-photon LIF spectra. © 2011 American Institute of Physics. [doi:10.1063/1.3615160]

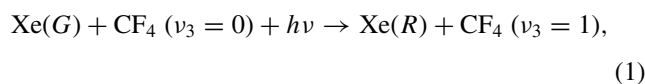
I. INTRODUCTION

Vacuum (Vac) UV spectra of pure Xe gas and of mixtures with lighter rare gases (Rg) have been a subject of several studies (Refs. 1 and 2 and references therein). Spectra of pure Xe show extended quasimolecular absorption on the red wings of the resonance lines corresponding to transitions from the repulsive ground state of Xe–Xe pairs to strongly bound excited states of Xe₂^{*}. In contrast, the Xe–Rg' interaction potentials correlating with the lowest Xe resonance states are strongly repulsive due to repulsion of the Rydberg electron from the closed shell Rg' atom (Pauli repulsion). The pressure-broadened resonance bands in Xe/Rg' mixtures are therefore degraded to the blue. Besides the transitions on the wings of resonance lines, spectra of Xe and Xe/Rg' mixtures also show quasimolecular transitions correlating with dipole-forbidden states of the Xe atom.

In comparison to other molecular gases, perfluoromethane has peculiar properties which support the observation of collision-induced transitions in absorption and luminescence excitation spectra of Rg/CF₄ mixtures (Rg = Xe, Kr). This gas is transparent in the Vac UV region up to $\lambda \sim 115 \text{ nm}$. Furthermore, collisions with CF₄ do not deactivate high lying excited states of the Xe and Kr atoms but efficiently transfer population to the lowest Xe 6s[3/2]₂ and Kr 5s[5/2]₂

metastable states. The metastable atoms decay following thermal activation to the resonance states lying $\sim 1000 \text{ cm}^{-1}$ higher in energy.

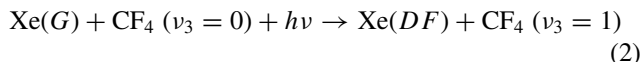
Early studies of Xe/CF₄ and Kr/CF₄ mixtures in the Vac UV region revealed strong quasimolecular absorption on the blue wings of Rg ns[3/2]₁ resonance lines and satellite transitions shifted $\sim 1000 \text{ cm}^{-1}$ further to the blue (Ref. 3 and references therein). In comparison to mixtures with light rare gases,^{1,2} blue wing absorption in mixtures with CF₄ covers a broader spectral region implying stronger repulsion between excited atom and molecule. The early studies³ were conducted with low spectral resolution. Recently, Xe/CF₄ and Kr/CF₄ was studied at high spectral resolution including the $\lambda < 120 \text{ nm}$ region which was omitted in Ref. 3 due to low intensity of the discharge light source. The high resolution data proved the assignment of satellites of resonance transitions (SRs) to vibrationally excited state of the collisional complex.⁴ The SRs are shifted from their parent resonance transitions by one quantum energy of the IR active ν_3 -mode of CF₄. The corresponding photoprocess may be written as follows:



where *G* and *R* denote the ground and a resonance states, respectively. Furthermore, the high resolution studies revealed numerous spectrally narrow satellites of dipole-forbidden transitions (SDFs) in the Xe atom.⁵ These satellites are also

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induced by the ν_3 -mode and correspond to

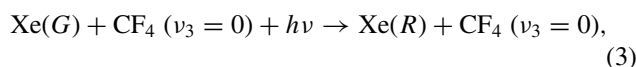


photoprocess, where DF denotes a dipole-forbidden state which cannot be accessed optically from the ground state.

Although processes (1) and (2) are formally similar, the mechanisms for borrowing transition strength are different for SR and SDF. The following conclusions concerning the differences between SR and SDF have been derived:⁵

- (i) SR are spectrally broad bands closely resembling in shape their parent pressure-broadened resonance bands. It implies that SRs correspond to transitions at small distances between atom and molecule, where $\text{Xe}(G)\text{--CF}_4$ ($\nu_3 = 0$) and $\text{Xe}(R)\text{--CF}_4$ ($\nu_3 = 1$) interaction potentials are not parallel. In contrast, spectrally narrow SDF bands (FWHM ~ 10 cm⁻¹) closely match the asymptotic energies of the $\text{Xe}(DF) + \text{CF}_4$ ($\nu_3 = 1$) collisional pair implying transitions at large distances, where $\text{Xe}(G)\text{--CF}_4$ ($\nu_3 = 0$) and $\text{Xe}(DF)\text{--CF}_4$ ($\nu_3 = 1$) interaction potentials are nearly parallel.
- (ii) SDF are much more intense in comparison to SR. The absorption cross section for the most intense SDFs reaches 10^{-35} cm⁵, and therefore, these bands are already seen in mixtures containing only few mbar of Xe and CF₄. The SR absorption cross section for comparison is $\sim 10^{-38}$ cm⁵.

Intense SDFs are usually observed on the wings of pressure-broadened resonance transitions.⁵ These bands are especially strong when $\text{Xe}(R \leftrightarrow DF)$ is a dipole allowed transition. This effect may be explained by an intensity borrowing from the resonance transition,



induced by interaction of $\text{Xe}(R \leftrightarrow DF)$ and CF_4 ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) transient dipoles. The dipole–dipole interaction matrix element is given by

$$\alpha = \langle \Psi_{DF} | U_{\text{dd}} | \Psi_R \rangle = \mu_{R \leftrightarrow DF} \mu_{\nu_3} \Phi / R^3,$$

where $\Psi_{DF} = \psi_{\text{Xe}(DF)} \psi_{\text{CF}_4(\nu_3 = 1)}$ and $\Psi_R = \psi_{\text{Xe}(R)} \psi_{\text{CF}_4(\nu_3 = 0)}$ are wavefunctions of dipole-forbidden and resonance states written as products of atomic and molecular wavefunctions, $\mu_{R \leftrightarrow DF}$ and μ_{ν_3} are the dipole moments of atomic and molecular transitions, Φ is a factor depending on the angular orientation of the instantaneous dipoles, and R is the distance between atom and molecule. The upper state wavefunction of Eq. (2) may be written as $c_{DF} \Psi_{DF} + c_R \Psi_R$. For a large R when $\alpha \ll \Delta$, we have $c_{DF} \sim 1$ and $c_R \sim \alpha / \Delta$, where Δ is the energy gap between $\text{Xe}(DF) + \text{CF}_4$ ($\nu_3 = 1$) and $\text{Xe}(R) + \text{CF}_4$ ($\nu_3 = 0$) states. The dipole moment of Eq. (2) is given by

$$\mu_{G \leftrightarrow SDF} = \langle c_{DF} \Psi_{DF} + c_R \Psi_R | \mu_{G \leftrightarrow R} | \Psi_G K \rangle \sim (\alpha / \Delta) \mu_{G \leftrightarrow R},$$

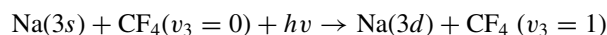
where $\Psi_{GS} = \psi_{\text{Xe}(G)} \psi_{\text{CF}_4(\nu_3 = 0)}$, and $\mu_{G \leftrightarrow R}$ is the dipole moment of the resonance transition. If the difference in energies of Eqs. (2) and (3) is neglected, the SDF absorption cross

sections are given by

$$\sigma_{\text{SDF}} \approx (\alpha / \Delta)^2 \sigma_R, \quad (4)$$

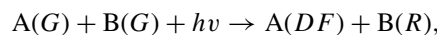
where σ_R is the atomic resonance absorption cross section. For strong resonances, $\sigma_R \sim 10^4$ Å² and SDF are readily seen when $(\alpha / \Delta)^2$ is only $\sim 10^{-4}$.

Similar satellites due to IR active modes of molecules may be observed in spectra of other atomic gas–molecular gas mixtures. Studies of Xe/C₂F₆ mixtures revealed satellites due to IR active ν_{10} -mode of C₂F₆.⁵ Like the ν_3 -mode of CF₄, this mode is related to stretch of the C–F bond. The energy difference ν_3 (CF₄)– ν_{10} (C₂F₆) is only 30 cm⁻¹ and the corresponding energy shift in positions of spectrally narrow SDF bands is clearly seen in high resolution spectra.⁵ An accidental proximity of atomic $R \leftrightarrow DF$ and IR active vibrational transitions may be found for many atom molecule pairs. In particular, the Na ($3p_{3/2,1/2} \leftrightarrow 3d_{5/2,3/2}$) and CF₄ ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) transition energies differ by 180 cm⁻¹. It has been demonstrated that the

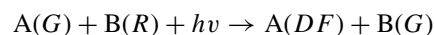


process is readily observed in LIF spectrum of Na/CF₄ mixture in a static cell.⁶ Simultaneous optical excitation of Na and CF₄ has been studied in further details in a crossed beam experiment.⁷ Excited Na atoms were preferably found at small scattering angles implying excitation at large impact parameter which is consistent with the long-range character of the dipole–dipole interaction.

Processes in which absorption or emission of one photon changes quantum states of two particles are known from studies of other binary systems. Excitation of two ground states atoms,



has been observed in spectra of mixtures of IA–IIIA group metals (Cs, Rb, Cs–Rb, Ba, Ba–Tl).^{8,9} Collisions of a ground state atom with an optically excited resonance state atom



(radiative collisions,¹⁰ laser induced collisional energy transfer¹¹) have been studied as well. Simultaneous vibrational excitation of two molecules has been observed in high pressure mixtures of molecular gases, cryogenic liquids, and molecular layers adsorbed on a surface (Refs. 12 and 13 and references therein). Vibrational satellites of atomic transitions have been reported in absorption and luminescence spectra of atom doped molecular solids.^{14–16}

Our previous paper on vibrationally induced transitions in Vac UV spectra of Xe/CF₄ mixtures⁵ was focused on a narrow 88 000–90 500 cm⁻¹ range around the Xe $6d[3/2]_1$ resonance. In the present paper, we investigate vibrational satellites in further detail. The above conclusions on the origin of satellite bands are verified for a large manifold of Xe transitions in a broad range from 68 000 cm⁻¹ (the first Xe resonance line) up to 95 000 cm⁻¹ (the LiF window cutoff). The Xe atom energy level diagram in Fig. 1 serves as a guide through the complex spectra (the range around Xe $6d[3/2]_1$ is omitted). In Sec. III A, we present results on SR in the region of the Xe $6s$, $6s'$, and $7s$ resonance states (left-hand side of Fig. 1) and discuss spectral similarities of the Xe $6s[3/2]_1$

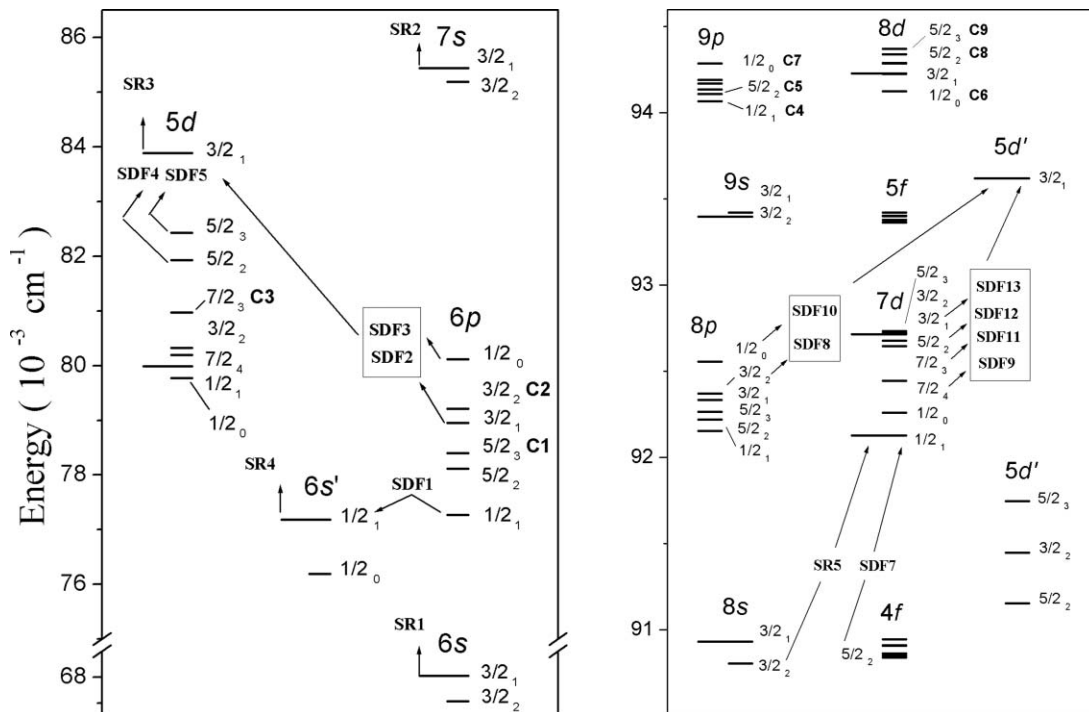


FIG. 1. The Xe atom energy levels diagram (Ref. 17) in the jl -coupling notation, $n[K]J$, where $K = j(5p^5) + l(nl)$ and $J = K + 1/2$; the $j(5p^5) = 1/2$ ion-core states have index prime. The 86 000–90 000 region is omitted. Resonance states are shown by longer lines. Observed transitions to dipole-forbidden states due to collision-induced breakdown of optical selection rules are labeled C1–C9. Observed satellites of resonance transitions are shown by vertical arrows and labeled SR1–SR5. Satellites of dipole-forbidden transitions are shown by arrows pointing toward the enhancing resonance state and labeled SDF1–SDF13.

SR and the Kr $5s[3/2]_1$ SR. Then, we go up consecutively in energy starting with the Xe $5d[1/2]_1$ resonance region in Sec. III B. Besides SR and SDF, the spectra in this region also show intense quasimolecular bands related to dipole-forbidden states of the Xe atom. The upper states of these transitions correlate with Xe(DF) + CF₄ ($\nu_3 = 0$). Their parent states are labeled C1–C9 in Fig. 1. In Sec. III C, we discuss the spectrum near the strong Xe $5d[3/2]_1$ resonance (left-hand side of Fig. 1). The region of high lying Xe $8s$, $7d$, $5d'$, and $8d$ states (right-hand side of Fig. 1) is considered in Sec. III D. The abbreviations in Fig. 1 are used in all figures and in the text. Section III E concerns with studies of Xe/C₂F₆ mixtures. Finally, in Sec. III F, we discuss two-photon LIF spectra of Xe/CF₄ and Xe/C₂F₆ mixtures and show an example of a vibrational satellite of the Xe $6p[1/2]_0$ two-photon resonance state.

II. EXPERIMENTAL

The experiments were conducted at the synchrotron radiation facility BESSY using a 10-m normal incidence monochromator.¹⁸ The cell was constructed from a standard CF65 cross-shape vacuum connector (Leybold) and was separated from the high vacuum part of the experimental setup by LiF windows. Rare gases and CF₄ (Linde) were used without further purification. Transmitted light was detected by a GaAs photodiode or by a photomultiplier tube (PMT) installed behind a screen covered with sodium salicylate luminophore. Absorption spectra of pure Xe and Kr at low pressure (<1 mbar) were used for the absolute wavelength calibration. The accuracy is ~ 0.5 cm⁻¹. The absorption cross section (σ) of

Xe-CF₄ collisional pairs was derived from the intensity (I), the cell length (L), and the partial pressures according to the Lambert-Beer law,

$$I = I_0 \exp(-\sigma L [\text{Xe}][\text{CF}_4]).$$

Undispersed emission of Rg/CF₄ mixtures excited by SR radiation was detected via side-on windows. One window was made of MgF₂ to observe emission in the Vac UV range with use of a solar blind photomultiplier, which is sensitive in the 114–350 nm region. Emission in the UV and visible spectral ranges was recorded via the second on-side window with the use of another photomultiplier.

Side-on photomultipliers accept luminescence excited in the spatial region near the cell center. When absorption is strong (for example, near the resonance wavelength), only a small fraction of SR flux reaches the cell center. To increase the luminescence intensity in the cell center, the entrance window was mounted close to the center with use of a special adapter attached to the entrance flange of the cell.

III. RESULTS AND DISCUSSION

A. Resonance ns and ns' transitions of Xe and Kr atoms

Shapes of pressure-broadened Xe $6s[3/2]_1$ and Kr $5s[3/2]_1$ resonances in mixtures with CF₄ and C₂F₆ have been discussed in some details in Ref. 19. Figure 2(a) shows spectra of Xe (1) and Kr (2) in mixture with CF₄. In terms of spectral width and structural features (typically one or two shoulders), these spectra are similar. The red wing absorption covers ~ 50 cm⁻¹ and is already seen at relatively small CF₄ pressures of

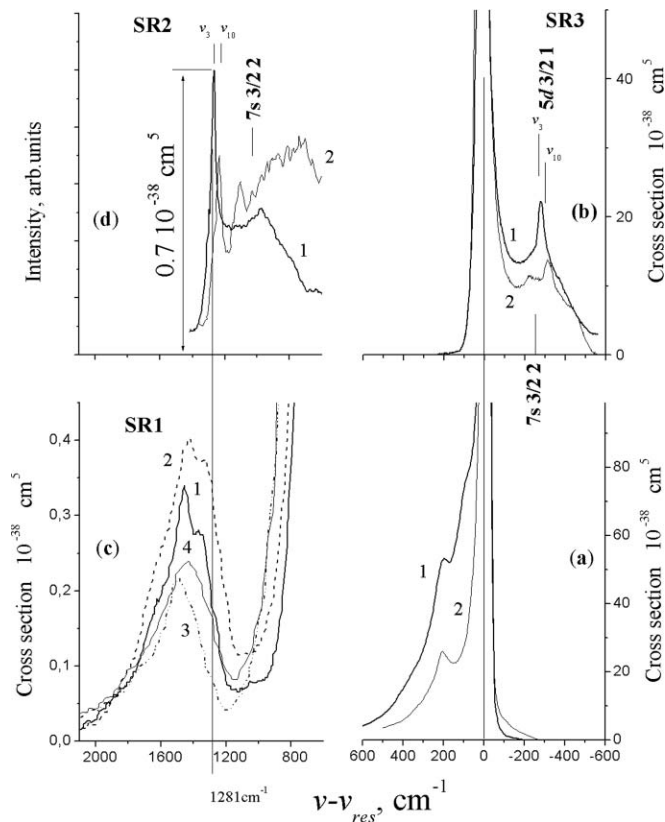


FIG. 2. (a) The Xe $6s[3/2]_1$ (1) and Kr $5s[3/2]_1$ (2) resonances in mixture with CF_4 , (b) the Xe $7s[3/2]_1$ resonance in mixture with CF_4 (1) and C_2F_6 (2), (c) satellite of Xe $6s[3/2]_1$ (1) in mixture with CF_4 , (d) satellite of Xe $7s[3/2]_1$ in luminescence excitation spectra of mixtures with CF_4 (1) and C_2F_6 (2). Panel (c) also shows satellite of Xe $6s[3/2]_1$ in mixture with C_2F_6 (2), and satellites of Kr $5s[3/2]_1$ in mixtures with CF_4 (3) and C_2F_6 (4). The lower sticks in (b) indicates the energy of Xe $7s[3/2]_2$ (relative to Xe $7s[3/2]_1$) and the upper sticks in (b) and (d) indicate energies of Xe $5d[3/2]_1$ and Xe $7s[3/2]_1$ increased by the vibrational quantum energy of ν_3 -mode of CF_4 ($\nu_3 = 1281 \text{ cm}^{-1}$) and ν_{10} -mode of C_2F_6 ($\nu_{10} = 1251 \text{ cm}^{-1}$). Some spectra for this Figure are taken from Refs. 4 and 19. Reprinted with permission from AIP Conf. Proc. Copyright 2008 American Institute of Physics.

about 10 mbar. The absorption continuum on the blue wing appears at higher pressures and covers $\sim 500 \text{ cm}^{-1}$ of spectral width.

Like Rg atoms, CF_4 possesses no positive electron affinity.²⁰ Thus, this blue wing broadening of the first Rg $ns[3/2]_1$ resonances is likely due to repulsion of the excited atomic Rydberg electron from the closed shell molecular system (Pauli repulsion). This type of interaction is known for heteronuclear $\text{Rg}^*-\text{Rg}'$ dimers, where it results in maxima on $\text{Rg}^*-\text{Rg}'$ potentials.²¹ As noted in Sec. I, this blue wing broadening in mixture with CF_4 covers a broader spectral region in comparison with Rg'/Rg mixtures. The binding in CF_4 is strongly ionic. According to *ab initio* calculations, a charge which is approximately equivalent to the charge of one electron is transferred from the central carbon atom to fluorine atoms.²² It is likely that the stronger repulsive interaction between Rg^* and CF_4 in comparison with the $\text{Rg}^*-\text{Rg}'$ case is due to this extra negative charge on the fluorine atoms around the carbon core.

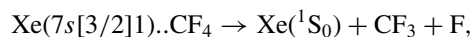
Due to the delocalization of the Rydberg electron density, the Pauli repulsion decreases with increase of the principal quantum number and the interaction potential becomes

attractive owing to attraction to the ion core. Spectra of Xe $6s[3/2]_1$ and Xe $7s[3/2]_1$ in Figs. 2(a) and 2(b) nicely illustrate this tendency. As is seen, the increase of principal quantum number by one changes the interaction from repulsive for Xe $6s[3/2]_1$ to attractive for Xe $7s[3/2]_1$ with an inverted wing structure. A similar effect is observed for the Xe *nd* resonance states discussed in Sec. III C.

Spectra of pressure-broadened resonances were recorded at a Xe pressure ~ 1 mbar and few hundred mbar of CF_4 . Observation of SRs corresponding to process (1) requires a higher Xe partial pressure, typically $\sim 10\text{--}50$ mbar. An absorption spectrum for the Xe $6s[3/2]_1$ satellite is shown in Fig. 2(c) (spectrum 1). The Xe $7s[3/2]_1$ SR (SR2) in a luminescence excitation spectrum is displayed in Fig. 2(d) (spectrum 1, absorption scale is indicated by the vertical arrow). The CF_4 gas is transparent in this spectral region and absorption and luminescence excitation spectra are nearly identical in shape.

As can be seen from Fig. 2, the SRs resemble their parent bands in shape. The shift between the red wings of the Xe $6s[3/2]_1$ resonance band and its satellite and the shift between the blue wings of the Xe $7s[3/2]_1$ resonance band and its satellite closely match the energy of the CF_4 vibrational quantum $\nu_3 = 1281 \text{ cm}^{-1}$. For the Xe $6s[3/2]_1$ state, the interaction potential is repulsive, and following optical excitation, the collisional complex dissociates yielding a resonance state atom and a vibrationally excited molecule. In contrast, transitions on the red wing of the Xe $7s[3/2]_1$ resonance or its satellite terminate at bound states. The width of these bands shows that the binding energy is at least $\sim 500 \text{ cm}^{-1}$ or larger considering that for collisions at room temperature energies, only a part of the upper bound potential is optically accessible from the repulsive ground state.

Luminescence excitation spectra of Xe/ CF_4 mixtures are similar in shape to the absorption spectra. There is no noticeable change in the luminescence quantum yield of a Xe/ CF_4 mixture when the wavelength is tuned across the red wing of the Xe $7s[3/2]_1$ resonance or its SR. It implies that the process,



does not take place, although the excitation energy is well above the CF_3-F bond dissociation energy (5.6 eV). The $\text{Xe}(7s[3/2]_1) \cdot \text{CF}_4$ bound complex likely decays either spontaneously (predissociation or radiative decay) or in collisions with CF_4 yielding lower lying excited states of the Xe atom.

The Xe $7s[3/2]_1$ SR may have contributions from two different coupling mechanisms. The sharp blue feature (Fig. 2(d)) matching the asymptotic energy of Xe $7s[3/2]_1 + \text{CF}_4$ ($\nu_3 = 1$) collision pair may be due to the long range coupling mechanism with the very strong Xe $5d[3/2]_1$ resonance (see transition strengths in Table I) via intermediate Xe *np* states. As shown in Secs. III B and III C, coupling with this resonance results in several other spectrally narrow satellites. In turn, the broad band shifted to the red from the asymptotic energy (Fig. 2(d)) may be due to the short range coupling mechanism similar to that which is responsible for the spectrally broad satellite of the Xe $6s[3/2]_1$ resonance (Fig. 2(c), spectrum 1).

TABLE I. Strengths of some transitions in the Xe atom (Ref. 23).

	S (a.u.)/transition energy (cm ⁻¹)				
	6s'[1/2] ₁	5d[1/2] ₁	5d[3/2] ₁	7s[3/2] ₁	7s[3/2] ₂
5p ⁶	1.31	0.03	4.29	0.21	
6p[1/2] ₁	12.9	20.6	0.2	1.47	22.5
6p[5/2] ₂	0.01	1.74	2.34	31.5	16.2
6p[3/2] ₁	0.57	0.57	30.4	31.2	2.45
6p[3/2] ₂	6.56	5.23	0.09	19.9	43.6
6p[1/2] ₀	1.86	0.77	35.2	16.1	

Table I lists strengths of some transitions in the Xe atom. As can be seen, the transitions from Xe 6p[3/2]₁ and Xe 6p[1/2]₀ to both the Xe 5d[3/2]₁ and Xe 7s[3/2]₁ resonance states have rather large strengths and these states may act as intermediate in the long range coupling mechanism. For the Xe 7s[3/2]₂ state, there are no coupling routes of comparable strength and this may explain the absence of a Xe 7s[3/2]₂ satellite (Fig. 2(d)). A case when both Xe ns states have satellites is discussed in Sec. III D.

Along with the Xe 6s[3/2]₁ SR in mixture with CF₄, Fig. 2(c) also shows, for comparison, the satellite of this resonance in mixture with C₂F₆ as well as satellites of the Kr 5s[3/2]₁ resonance in both mixtures. As can be seen, these bands have very similar blue graded shapes. The Kr 5s[3/2]₁ resonance (S = 0.718 a.u. (Ref. 23)) is a factor of 1.3 weaker than Xe 6s[3/2]₁. Satellite intensities correlate with transition strengths. The Kr 5s[3/2]₁ SR in both CF₄ and C₂F₆ mixtures is ~1.5 times weaker than the Xe 6s[3/2]₁ SR. Intensities also correlate with the intensities of vibrational transitions. The CF₄ ($\nu_3 = 0 \rightarrow \nu_3 = 1$) and C₂F₆ ($\nu_{10} = 0 \rightarrow \nu_{10} = 1$) transitions were calculated using the NIST Computational Chemistry Comparison and Benchmark Database.²⁴ The intensity ratio of ν_{10} to ν_3 was ~1.3 for all tested basis sets. The intensity ratio of SR in C₂F₆ to SR in CF₄ is close to this value (Fig. 2(c)). The Kr 5s'[1/2]₁ SR in mixture with CF₄ was also observed. This band is nearly identical in shape and intensity to the Kr 5s[3/2]₁ SR, as shown in Fig. 2(c) (spectrum 3). It should be noted in this respect that strengths of Kr 5s'[1/2]₁ (S = 0.678 a.u. (Ref. 23)) and Kr 5s[3/2]₁ (see above) are also nearly equal. Satellite of the corresponding Xe 6s'[1/2]₁ resonance is spectrally overlapped with other transitions in the Xe spectrum (see below).

The C₂F₆ molecules strongly absorb Vac UV radiation in the $\lambda < 120$ nm region which complicates studies (this was an obstacle for recording the Kr 5s'[1/2]₁ SR). On the other hand, collisions with C₂F₆ do not nonradiatively quench high lying Xe atom states but transfer population to the Xe 6s states, which decay radiatively. Therefore, some satellites of high lying states may still be seen in luminescence excitation spectra. Figure 2(d) shows Xe 7s[3/2]₁ SR in a luminescence excitation spectrum. Like in mixture with CF₄, this band has a sharp blue wing and the small shift due to the difference of ~30 cm⁻¹ in ν_3 and ν_{10} vibrational quanta is clearly seen. The onset of C₂F₆ absorption coincides spectrally with Xe 7s[3/2]₁ SR. The C₂F₆ absorption cross section in this region significantly increases as wavelength decreases, and as a re-

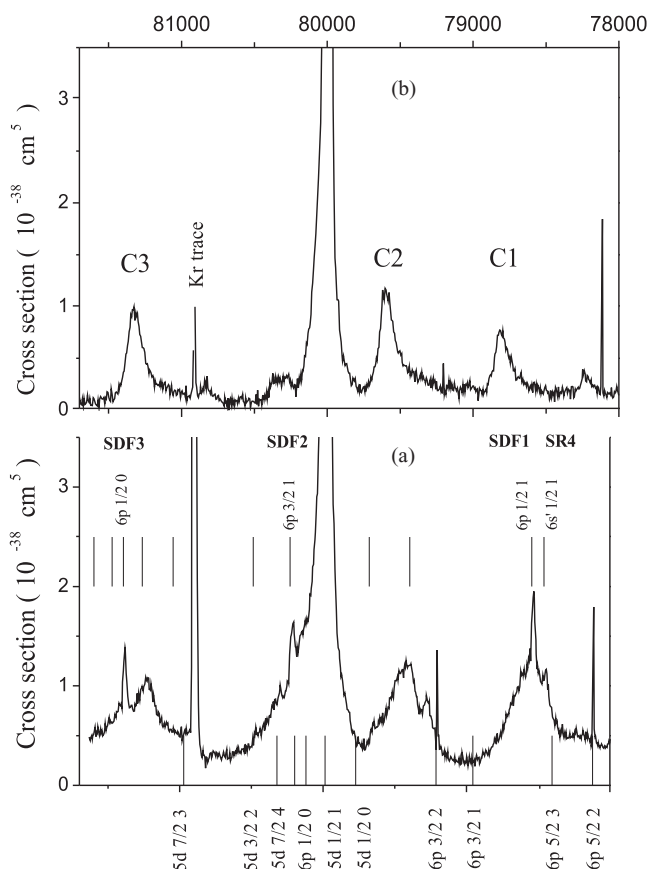


FIG. 3. Absorption cross section in the region of the Xe 5d[1/2]₁ resonance. Mixtures: Xe 5 mbar/CF₄ 800 mbar (a) and Xe 4 mbar/He 940 mbar (b). The lower sticks indicate the Xe atom level energies and the upper sticks indicate ν_3 satellites energies.

sult, the luminescence intensity on the blue wing of this satellite is partially suppressed by stronger absorption.

In conclusion of this section, we note that no satellite bands due to excitation of other vibrational modes of CF₄ and C₂F₆ were found in the present study. Hot bands originating from vibrationally excited Xe(G) + CF₄ ($\nu_3 = 1$) collision pairs were not observed as well. Experiments at elevated temperature might reveal such bands.

B. Xe 5d[1/2]₁ resonance state

The Xe 5d[1/2]₁ resonance is relatively weak and a higher partial pressure of Xe (typically few mbar) is needed to obtain a strong pressure-broadened band. Spectra of mixtures with CF₄ and He in the Xe 5d[1/2]₁ region are compared in Fig. 3. In mixture with CF₄ (Fig. 3(a)), the broadening effect is more pronounced on both wings of the Xe 5d[1/2]₁ resonance (absorption on the red wing in mixture with He is mainly due to Xe₂). The spectrum with He (Fig. 3(b)) displays several transitions to electronic states correlating with Xe(DF) states. The three most intense bands are labeled C1–C3. Similar red shaded bands have been observed in mixtures with Ne and Ar.^{1,2} Accepting the assignment suggested in Ref. 1, one finds that these bands are shifted by ~400 cm⁻¹ to the blue from their parent dipole-forbidden transitions. In the heavier Rg gases, the shift is smaller.¹

The spectrum with CF_4 (Fig. 3(a)) displays three similar collision-induced bands which are spectrally broader and less shifted to the blue in comparison with Rg gases. Transitions to vibrationally excited states of $\text{Xe}-\text{CF}_4$ complex need to be considered as well. As seen from Fig. 3(a), the band C1 is spectrally overlapped with the $\text{Xe } 6s'[1/2]_1$ satellite (SR4). Similar to the $\text{Xe } 6s[3/2]_1$ resonance (Fig. 2(a)), the $\text{Xe } 6s'[1/2]_1$ resonance in mixture with CF_4 is blue shaded (spectrum not shown) and, thus, the $\text{Xe } 6s'[1/2]_1$ SR is expected to be blue shaded and overlapped with band C1. The $\text{Xe } 6s'[1/2]_1$ SR is, however, too weak to resolve the shape, which is consistent with the following consideration. The $\text{Kr } 5s[3/2]_1$ and $\text{Kr } 5s'[1/2]_1$ resonances have nearly equal strengths and the intensities of their SRs are nearly the same (see Sec. III A). The $\text{Xe } 6s[3/2]_1$ and $\text{Xe } 6s'[1/2]_1$ resonances also have comparable strengths ($S = 1.36$ and 1.31 a.u. (Ref. 23)) and the same is expected for their SRs. Absorption cross sections for the $\text{Xe } 6s[3/2]_1$ SR and band C1 differ by a factor of 4 (compare band C1 in Fig. 3(a) with spectrum (1) in Fig. 2(c)) and, thus, the $\text{Xe } 6s'[1/2]_1$ SR is likely by a factor of 4 weaker than band C1.

The spectrum in Fig. 3(a) displays in addition several spectrally narrow bands which may be unambiguously assigned as satellites of dipole-forbidden transitions. The sharp SDF1 band on the top of band C1 is satellite of $\text{Xe } 6p[1/2]_1$. The $\text{Xe } (6p[1/2]_1 \leftrightarrow 6s'[1/2]_1)$ transition is strong (Table I) and SDF1 most likely borrows transition strength from the $\text{Xe } 6s'[1/2]_1$ resonance owing to mixing with the $\text{Xe } 6s'[1/2]_1 + \text{CF}_4$ ($\nu_3 = 0$) resonance state induced by interaction of transient dipoles (see Sec. I).

The other two narrow bands in Fig. 3(a) labeled SDF2 and SDF3 are satellites of $\text{Xe } 6p[3/2]_1$ and $\text{Xe } 6p[1/2]_0$, respectively. These transitions likely borrow strength from the $\text{Xe } 5d[3/2]_1$ resonance. As can be seen from Table I, both the $\text{Xe } (6p[3/2]_1, 6p[1/2]_0 \leftrightarrow 5d[3/2]_1)$ transitions are strong. In turn, the weakness of $\text{Xe } (6p[3/2]_2, 6p[5/2]_2 \leftrightarrow 5d[3/2]_1)$ transitions explains the absence of the corresponding SDFs. The $\text{Xe } 5d[1/2]_1$ resonance is very weak and cannot be a source of transition strength neither for own SR nor for $\text{Xe } 6p$ SDFs

C. $\text{Xe } 5d[3/2]_1$ resonance state

Figure 4 shows some spectra in the region of the $\text{Xe } 5d[3/2]_1$ resonance. The resonance band itself is blue shaded (spectrum 1) implying a repulsive interaction with CF_4 . In contrast, the $\text{Xe } 6d[3/2]_1$ band is red shaded⁵ and, thus, similar to the $\text{Xe } 6s/7s$ pair (Fig. 2(a) and 2(b)), an increase of the principal quantum number by one changes the interaction from repulsive to attractive.

The sharp SDF4 and SDF5 bands in Fig. 4 are unambiguously assigned as ν_3 satellites of $\text{Xe } 5d[5/2]_2$ and $\text{Xe } 5d[5/2]_3$. For comparison, Fig. 4 shows the spectrum of a mixture with C_2F_6 . The shift in SF5 corresponding to the energy difference $\Delta = \nu_3(\text{CF}_4) - \nu_{10}(\text{C}_2\text{F}_6) = 30 \text{ cm}^{-1}$ is clearly seen. In contrast to $\text{Xe } 6p$ SDFs discussed in Sec. III B, the $\text{Xe } 5d$ SDFs are a second order effect of electric field induced mixing between forbidden and resonance states with the $\text{Xe } np$ states acting as intermediate. No such SDFs are seen in the region

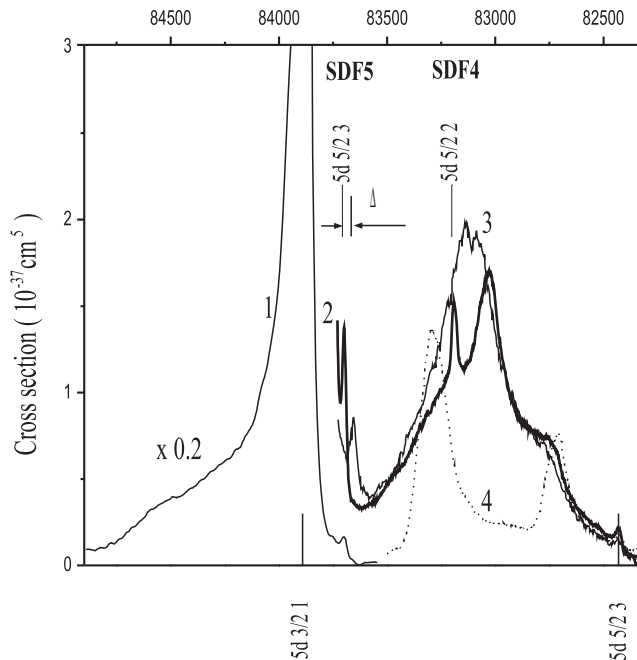
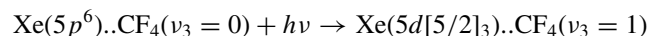


FIG. 4. Absorption cross section near the $\text{Xe } 5d[3/2]_1$ resonance. Mixtures: $\text{Xe } 1 \text{ mbar}/\text{CF}_4$ 300 mbar (1, multiplied by 0.2), $\text{Xe } 5 \text{ mbar}/\text{CF}_4$ 230 mbar (2), $\text{Xe } 5 \text{ mbar}/\text{C}_2\text{F}_6$ 300 mbar (3), $\text{Xe } 5 \text{ mbar}/\text{He}$ 260 mbar (4). The lower sticks indicate energies of the Xe atom levels and the upper sticks indicate energies of the Xe atom levels increased by ν_3 quantum energy. $\Delta = \nu_3(\text{CF}_4) - \nu_{10}(\text{C}_2\text{F}_6) = 30 \text{ cm}^{-1}$. The gap between two bands in the spectrum of mixture with He is approximately the same energy as between $\text{Xe } 5d[5/2]_3$ and $\text{Xe } 5d[5/2]_2$ states (the latter is not on the plot scale).

of the $\text{Xe } 5d[1/2]_1$ resonance (Fig. 3) and their appearance near $\text{Xe } 5d[3/2]_1$ (Fig. 4) is due to the large strength of this resonance (Table I).

The very strong $\text{Xe } 5d[3/2]_1$ resonance may have a satellite. Indeed, the band labeled SR3 in Fig. 2(b) closely matches with the energy of the $\text{Xe } 5d[3/2]_1$ SR. The $\text{Xe}/\text{C}_2\text{F}_6$ mixture spectrum in Fig. 2(b) displays a similar band which is shifted to the red due to the difference in ν_3 and ν_{10} energies. It should be noted, however, that in contrast to the spectrally narrow SDFs, SR3 does not match exactly the asymptotic energy of $\text{Xe } 5d[3/2]_1 + \text{CF}_4$ ($\nu_3 = 1$) (or C_2F_6 ($\nu_{10} = 1$)) pair. In both mixtures, SR3 is shifted by $\sim 10 \text{ cm}^{-1}$ to the red, while the parent resonance band is graded to the blue (Fig. 4(a)). A tentative explanation of this shift is an interaction of the resonance dipole with the dielectric continuum which also causes the broadening on the red wing on the $\text{Xe } 5d[3/2]_1$ resonance (Fig. 4).

The broad band centered at $\sim 83\,100 \text{ cm}^{-1}$ in Fig. 4 is related to the $\text{Xe } 5d[5/2]_3$ state. The high intensity of this band in comparison with C1–C3 in Fig. 3 is likely due to the proximity to the strong $\text{Xe } 5d[3/2]_1$ resonance. It should be noted that the energy separation between the $83\,100 \text{ cm}^{-1}$ band and a broad shoulder on the blue side of the $\text{Xe } 5d[3/2]_1$ resonance is close to the ν_3 -quantum energy. The shoulder may be due to the



transitions at small impact parameters for which the upper and lower potentials are not parallel (in contrast to the spec-

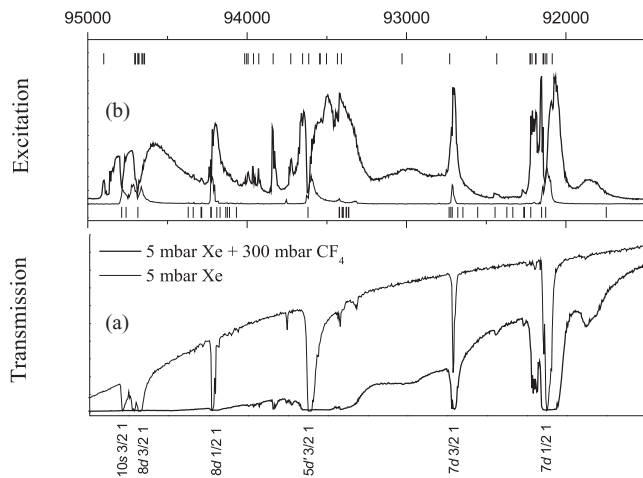
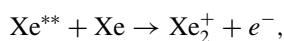


FIG. 5. Transmission (a) and luminescence excitation (b) spectra of Xe and Xe/CF₄ mixture. The lower sticks indicate Xe levels, the upper sticks are the Xe levels displaced by the energy of CF₄ ν₃ quantum.

trally narrow Xe 5*d*[5/2]₃ SDF corresponding to a transition between nearly parallel potentials).

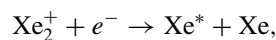
D. High-lying states of Xe atom in the λ < 110 nm region

In our previous work,⁵ we discussed Xe/CF₄ spectra in the 88 000–91 500 region covering the Xe 8*s*[3/2]₁ and Xe 6*d*[3/2]₁ resonances. Figure 5 shows an overview of transmission (a) and luminescence excitation (b) spectra further to the blue. The entrance window of the solar blind PMT is made of Mg₂F. The transmission threshold of this material is at ~88 000 cm⁻¹ (λ ~114 nm). Therefore, the signal in the excitation spectrum in Fig. 5(b) is due to emission from lower lying resonance states populated collisionally. An alternative mechanism is associative ionization,



(threshold energy for this process is 90 150 cm⁻¹ (Ref. 25)) followed by ion-electron recombination or dissociative

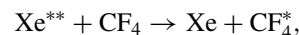
attachment,



in subsequent ion-electron encounters. This process predominantly populates Xe 6*p* and Xe 5*d* states²⁶ and collisions transfer population to the lowest Xe 6*s*[3/2]₁ resonance state.

In mixtures with CF₄, the luminescence signal is stronger than in pure Xe (Fig. 5(b)). This enhancement may be in part due to a more complete population transfer to lower lying states which decay radiatively in the λ > 114 nm region, where the PMT is sensitive. Another contribution may be the recombination process Xe* + Xe + CF₄ → Xe₂* + CF₄. The Xe₂* dimers decay at λ ~175 nm where the sensitivity of the solar blind PMT is likely higher than at shorter wavelengths.

As can be seen from Fig. 5(a), CF₄ itself absorbs Vac UV radiation in this region and the cross section increases with photon energy. This absorption indicates that acceptor states for an intermolecular energy transfer,



are available. In collisions with He, the intermolecular energy transfer is excluded and population from Xe^{**} states may only be transferred to the lowest excited Xe 6*s* states. Experiments showed that for the same pressures, luminescence signals from Xe/CF₄ and Xe/He are comparable. It implies that the probability of intermolecular transfer in Xe^{**} + CF₄ collisions is small in comparison with relaxation to lower lying states.

Spectra in Fig. 5 display numerous SDFs along with the pressure-broadened resonance transitions. Satellites of Xe 4*f* and Xe 8*s* states appear near the Xe 7*d*[1/2]₁ resonance. A striking example of the SDF effect is seen on the blue side of the strong Xe 5*d*'[3/2]₁ resonance. These spectral regions are shown in detail with high resolution in Figs. 6 and 7.

Figure 6(a) presents satellites of dipole-forbidden Xe 8*s*[3/2]₂ and Xe 4*f*[5/2]₂ states (SDF6 and SDF7) and a satellite of the Xe 8*s*[3/2]₁ resonance state (SR5) all near the Xe 7*d*[1/2]₁ resonance. The SDF7 is a first order effect because the parent state is coupled optically with Xe 7*d*[1/2]₁. In contrast to the spectrally broad Xe 6*s*[3/2]₁ SR (SR1 in Fig. 2),

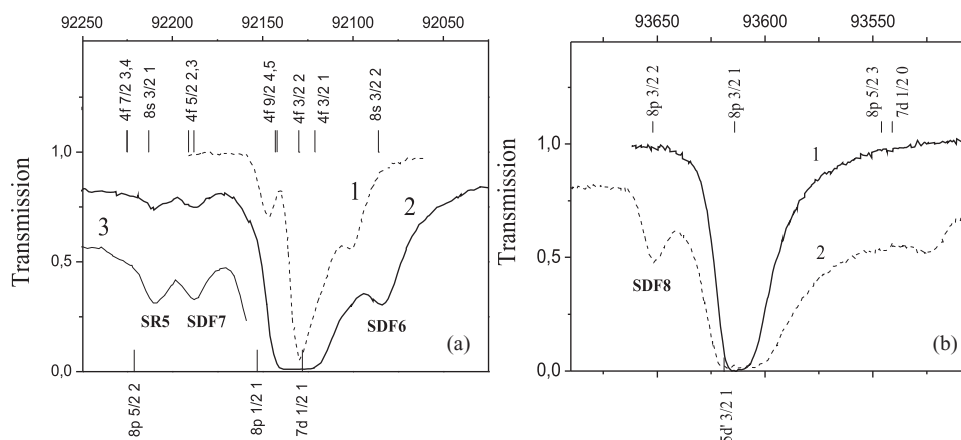


FIG. 6. (a) Transmission spectra near the Xe 7*d*[1/2]₁ resonance: 3 mbar Xe (1), 1.3 mbar Xe/60 mbar CF₄ (2), 3 mbar Xe/130 mbar CF₄ (3). (b) Transmission spectra near the Xe 5*d*'[3/2]₁ resonance: 2 mbar Xe (1), 2 mbar Xe/15 mbar CF₄ (2). Absorption cross section at the maximum of the Xe 8*p*[3/2]₂ SDF is ~5 × 10⁻³⁶ cm⁵.

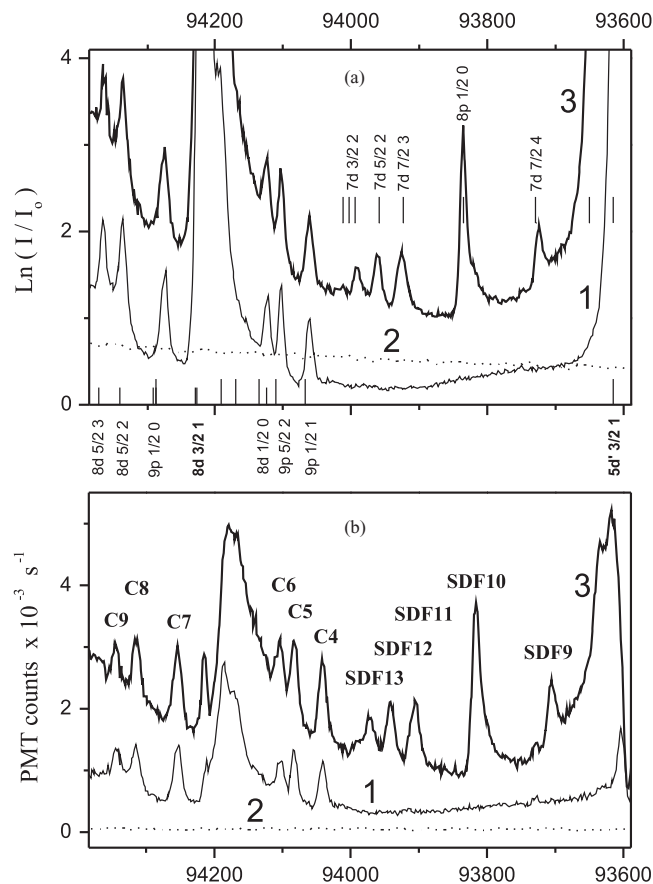


FIG. 7. Absorption (a) and luminescence excitation (b) spectra of Xe 35 mbar (1), CF₄ 70 mbar (2), and Xe 35 mbar + CF₄ 70 mbar (3). Undispersed luminescence was recorded by a solar blind PMT. The lower set of sticks shows energies of Xe atom levels and the upper set of sticks shows the energies of lower lying Xe levels displaced by the ν_3 quantum energy.

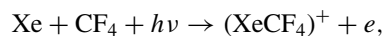
SR5 is a narrow band which matches the asymptotic energy of the collisional pair. As noted in Sec. I, SR of the lowest resonance states correspond to transitions at small impact parameter and they differ from SDF in terms of the intensity borrowing mechanisms. SR5 is likely a second order effect in electric field mixing induced by the CF₄ vibrational dipole similar to SDF6 and other SDFs with parent states not directly coupled with the resonance states.

Figure 6(b) displays the Xe 8p[3/2]₂ SDF (SDF8) near the Xe 5d'[3/2]₁ resonance. SDF8 is very strong with an absorption cross section at maximum of $\sigma \sim 5 \times 10^{-36}$ cm⁵ and can be seen for partial pressures of Xe and CF₄ of only ~ 1 mbar. Several weaker SDFs in the region further to the blue from the Xe 5d'[3/2]₁ resonance are shown in Fig. 7. The satellite of Xe 8p[1/2]₀ (SDF10) is stronger than the Xe 7d SDFs (SF9, SF11–SF13) because its parent state is directly coupled with the Xe 5d'[3/2]₁ resonance. However, the difference in intensity is only a factor of 3–5 and the Xe 7d SDFs are readily seen for the same experimental conditions. In particular, the spectrum displays a satellite of Xe 7d[7/2]₄ (SDF9). This state may be coupled with the resonance states only in the fourth order of perturbative description of electric field induced mixing (a satellite of the lower lying Xe 6d[7/2]₄ state has also been observed⁵). As shown above for the Xe 6p satellites, at least qualitatively the intensities of these bands

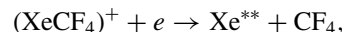
can be related to the strengths of transitions to the Xe 6s' [1/2]₁ and Xe 5d[3/2]₁ resonance states. Transition strengths between high lying Xe states are not known to date (some preliminary calculations have recently been performed²⁷).

The spectral region in Fig. 7 is ~ 4000 cm⁻¹ below the Xe atom ionization threshold, IP(Xe) = 97 873 cm⁻¹ (102.17 nm). In principle, interaction of transient dipoles may couple the Xe(DF) + CF₄ ($\nu_3 = 1$) states with optically accessible Xe(IC) + CF₄ ($\nu_3 = 0$) states in the ionization continuum (IC). Although the transitions to IC are weaker than to bound resonance states, this coupling mechanism may contribute to the optical dipole moment of SDF. Interestingly, if the energy gap between a given Xe(DF) state and the ionization threshold is less than the ν_3 quantum energy, the Xe(DF) + CF₄ ($\nu_3 = 1$) state would lie in the ionization continuum and the Xe(IC \leftrightarrow DF) and CF₄ ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) transitions would be in an exact resonance.

Another interesting question concerns the photoionization of Xe–CF₄ collisional pairs. As seen from Fig. 5, the luminescence excitation spectrum of mixtures with CF₄ display a continuum in the region on the blue side of the Xe 7d[3/2]₁ resonance at 107.86 nm. This continuum may be due to associative photoionization,



followed by dissociative attachment,



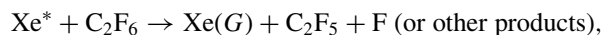
in subsequent ion-electron encounters. To our knowledge, the threshold energy for this process is not known to date.

Finally, yet another observation should be mentioned. To enhance the intensity of SDFs on the background of the continuous CF₄ absorption, the spectrum 3 in Fig. 7 was recorded at a high Xe pressure and a low partial pressure of CF₄. Spectra of pure Xe (1) and CF₄ (2) are also shown for comparison. As can be seen, the spectrum of pure Xe shows several narrow bands labeled C4–C9. These transitions are induced by collisions with Xe and the energies are close to Xe(DF) + Xe (G) asymptotic energies. Collisions with CF₄ and He only weakly affect intensities and shapes of these bands. It is likely that C4–C9 are due long range interaction of the Xe(DF) + Xe (G) states with states in the Xe₂ ionization continuum. To our knowledge, the Xe spectrum in this region is poorly known. More detailed spectroscopic and theoretical studies appear of interest.

E. Spectroscopy of Xe/C₂F₆ mixtures

Like CF₄, the C₂F₆ molecule has no electron affinity. Its IR spectrum displays a very intense and narrow band corresponding to the ν_{10} mode ($\nu_{10} = 1251$ cm⁻¹), and two weaker bands corresponding to ν_5 (1117 cm⁻¹) and ν_6 (714 cm⁻¹) modes.²⁸ The $\nu_{10}:\nu_5:\nu_3$ intensity ratio is approximately 10:3:1.

C₂F₆ is transparent in the $\lambda > 120$ nm region and mixtures containing ~ 1 bar of this gas can be studied. Similar to CF₄, C₂F₆ efficiently transfers population between excited states of the Xe atom while the nonradiative quenching,



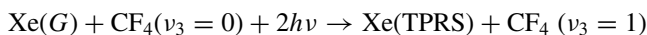
is weak or absent. The quantum yields of Vac UV luminescence following excitation of Xe/CF₄ and Xe/C₂F₆ mixtures in the $\lambda > 120$ nm region are nearly the same.

The shapes of pressure-broadened resonance transitions and their satellites in Xe/C₂F₆ and Xe/CF₄ mixtures are similar, as in particular, was demonstrated above for satellites of resonance Xe 6s[3/2]₁ and Kr 5s[3/2]₁ transitions (Fig. 2(c)). The difference in vibrational quanta energies $\Delta = \nu_3(\text{CF}_4) - \nu_{10}(\text{C}_2\text{F}_6) = 30 \text{ cm}^{-1}$ is hardly seen for these spectrally broad satellites. In contrast, for the spectrally narrow satellites, the shift is well resolved. Examples are shown in Figs. 2(d) and 4.

Experiments with Xe/C₂F₆ mixtures conducted in the course of the present study were less extensive in comparison with Xe/CF₄ because of the strong absorption in the spectrally rich $\lambda < 120$ nm region. These experiments were mainly aimed to confirm the main findings for Xe/CF₄. It should be noted that like CF₄ and C₂F₆, more complex perfluorocarbons (C₃F₈, C₄F₁₀) have a similar intense and spectrally narrow absorption band in the IR region.²⁸ This band is related to the stretch of the C–F bond and is close to 1300 cm^{-1} for all C_nF_{2n+2} molecules. Strong absorption of the polyatomic molecules in the Vac UV region is an obstacle for studies of collision induced effects in spectra of mixtures with Xe. However, systematic studies with a more extended set of C_nF_{2n+2} gases may be conducted for Hg or other atoms for which transitions to high lying states or the ionization continuum are in the region where C_nF_{2n+2} gases are transparent.

F. Vibrational satellites in two-photon LIF spectra

The Xe $np[1/2]_0$, $np[3/2]_2$, and $np[5/2]_2$ states are coupled with the ground Xe 5p⁶ state by two-photon transitions. Similar to one-photon resonances, transitions to two-photon resonance states (TPRS) may have satellites corresponding to the process,



Furthermore, electric field induced mixing of two-photon resonance and two-photon forbidden states may cause satellites of two-photon forbidden transitions.

In the course of the present study, test experiments with two-photon excitation of mixtures of Xe with CF₄ and C₂F₆ were conducted. The fundamental frequency of a Lambda Physik dye laser pumped by a Lambda Physik excimer laser was doubled by a BBO-I crystal to obtain UV photons in the region of $40\,000 \text{ cm}^{-1}$. Gas mixtures were contained in a metal cell mounted on the entrance slit port of a 0.5 m vacuum monochromator (Minuteman). Laser induced luminescence in the Vac UV region was monitored via a side-on window by a solar-blind photomultiplier. The two-photon absorption cross sections is small and in comparison with the one-photon experiments, much higher partial pressures were required to observe weak bands. Typical mixtures consisted of ~ 1 bar of Xe and ~ 3 bar of CF₄ or C₂F₆. The emission spectra of these high-pressure mixtures display a broad Xe₂^{*} band centered at $\lambda \sim 175$ nm. At low pressure, the 147 nm resonance band of the Xe atom was seen, but the red-shifted satellite transition

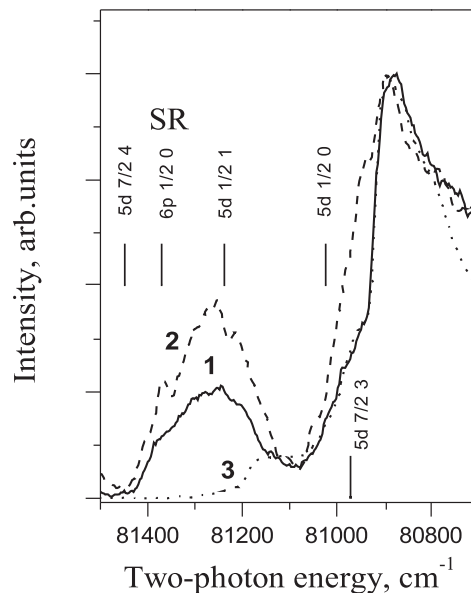
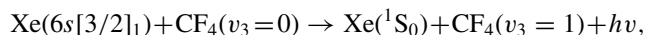


FIG. 8. Two-photon Vac UV luminescence excitation spectra: Xe 1 bar/CF₄ 2.5 bar (1), Xe 1 bar/C₂F₆ 2.5 bar (2), Xe 1 bar/Ar 2.5 bar (3). Luminescence was monitored at $\lambda \sim 175$ nm (maximum of Xe₂ emission band). The lower stick indicates the Xe 5d[7/2]₃ state energy, the upper sticks indicate energies of lower lying states shifted by ν_3 quantum energy of CF₄.

to the vibrationally excited ground state,



was not found in these spectra.

Figure 8 shows excitation spectra on the blue wing of the Xe 6p[1/2]₀ two-photon resonance (one photon spectrum in this region is shown in Fig. 4). The resonance band is saturated at these high pressures and is not shown in Fig. 8. The band around $80\,800 \text{ cm}^{-1}$ is seen in all mixtures and is likely related to the two-photon forbidden Xe 5d[7/2]₃ state. In contrast, the band around $81\,300 \text{ cm}^{-1}$ is not seen in mixture with Ar. This band is close to the energy of the Xe 6p[1/2]₀ two-photon resonance state increased by one vibrational quantum energy of CF₄ (C₂F₆), and therefore, it is attributed to its vibrational satellite.

In the course of the present work, test LIF experiments in the region of the higher lying Xe 6p' and Xe 7p states were conducted as well. This region is especially interesting because numerous satellites of the Xe 7p and Xe 6d states were observed in one-photon spectra.⁵ Unfortunately, because of the small cross section for Xe 7p and Xe 6p' two-photon resonances and a decrease of the frequency-doubling efficiency, the LIF signal was too weak. Studies of two-photon excitation of jet-cooled Xe-CF₄ and Xe-C₂F₆ vdW molecules using sensitive REMPI detection might give interesting results.

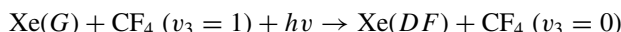
IV. CONCLUSION

Spectroscopic studies of Xe/CF₄ mixtures have shown that a strong IR active mode of a molecule may induce a large manifold of satellite transitions in the spectra of atom-molecule collision pairs. When the energy gap between Xe(R) and Xe(DF) is close to the ν_3 quantum energy and Xe(R \leftrightarrow DF) is an allowed optical transition, the Xe(DF) + CF₄ ($\nu_3 = 1$) and Xe(R) + CF₄ ($\nu_3 = 0$) states are mixed by the

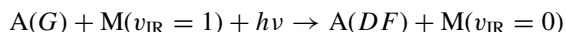
dipole-dipole interaction, and SDF acquires a very large strength. It is striking that some satellites are readily seen both in absorption and in luminescence excitation spectra for partial pressures of Xe and CF₄ in the gas cell around only 1 mbar.

Spectra also display numerous SDFs for which the parent states are not optically coupled with the resonance states. These SDFs may be explained as a higher order effect of electronic state mixing induced by the CF₄ ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) transient dipole.⁵ This mechanism seems not to be applicable for the spectrally broad satellites of the lowest resonance transitions in Xe and Kr atoms. The resonance states may be coupled with each other via intermediate np -states. In particular, Kr $5s[3/2]_1$ and Kr $5s'[1/2]_1$ SRs are nearly identical in shape and intensity, although the parent state of the latter SR is a factor of two closer to Kr $5p$ states which may act as intermediate. These bands are likely due to inelastic scattering of the Rydberg electron on the CF₄ molecule causing its vibrational excitation. This question requires further studies.

Owing to large ν_3 (CF₄) quantum energy, the population of $\nu_3 = 1$ level at room temperature is negligible which prevents observation of

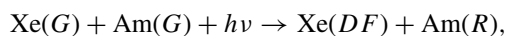


transitions corresponding to a vibrational deactivation of CF₄. These transitions would be strongly enhanced by mixing with a Xe(R) + CF₄ ($\nu_3 = 1$) resonance state, if the Xe(R) state is below Xe(DF) and the energy gap is $\sim \nu_3$ (CF₄). For example, this condition is met for the Xe $8s[3/2]_1$ resonance state and Xe $8p$ forbidden states (Fig. 1). In principle, the

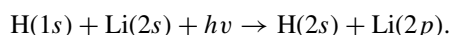


transition enhanced by proximity to a $A(R) + M(\nu_{\text{IR}} = 0)$ resonance may be used for optical cooling. Assuming that the gas mixture is in a cavity of a transparent matrix, and $M(\nu_{\text{IR}} = 0) \rightarrow M(\nu_{\text{IR}} = 1)$ and $A(DF) \rightarrow A(R)$ processes are due to energy transfer from/to matrix, the cooling effect would take place, if ν_{IR} is larger than the energy gap between $A(DF)$ and $A(R)$. Essential requirements are radiative decay of $A(R)$ in the transparency window of the matrix, stability of $A(R)$ in respect of collisional quenching, and relatively small ν_{IR} energy to ensure significant population at room temperature.

As noted in Sec. I, simultaneous optical excitation of two ground state atoms has been observed before.^{8,9} In context to the present studies in the Vac UV region, we mention that the process



where Am is an alkali atom, may be observed when the Am ($ns \leftrightarrow np$) resonance transition and Xe($R \leftrightarrow DF$) transition are close in energy, although continuous absorption to alkali ionization continuum would be a complication for such studies. Another interesting example of such a process in the Vac UV region is



The Li ($2s \leftrightarrow 2p$) energy is $\sim 330 \text{ cm}^{-1}$ less than that of H ($2s \leftrightarrow 3p$) and, the transition to H ($2s$) + Li ($2p$) is shifted by the same amount from the H ($1s \rightarrow 3p$) $L\beta$ resonance. Because of the large abundance of Li and H, this process is

of astrophysical interest and may also find applications for diagnostics of H rich plasmas employing a Li beam method (Ref. 29 and references therein). In a broader sense, $A(G) + B(G) + h\nu \rightarrow A(DF) + B(R)$ transitions enhanced by an accidental proximity of $A(DF \leftrightarrow R)$ and $B(G \leftrightarrow R)$ transitions may likely be found in spectra of other binary systems ranging from the deep IR to inner shell excitations in the x-ray region. Such processes may be of interest for light emitting technology to increase efficiency of broadband optical excitation of luminophores, optical cooling, monitoring transient species, and concentrations of their precursors and other applications.

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