Abstract

The frequency dependence of the multiple-photon resonances to the rotation-vibrational levels of the first two ν_3 overtones are calculated for SF_6 and SiF_4. From these calculations we can identify most of the features seen in the high intensity SF_6 absorption data and predict those features that would be seen in similar SiF_4 data.

PREDICTIONS OF MULTIPHOTON RESONANCES IN SF_6 AND SiF_4

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Received 13 July 1982

The frequency dependence of the multiphoton resonances to the rotation-vibrational levels of the first two ν_3 overtones are calculated for SF_6 and SiF_4. From these calculations we can identify most of the features seen in the high intensity SF_6 absorption data and predict those features that would be seen in similar SiF_4 data.

The high-intensity absorption and photodissociation spectra of SF_6 recently reported by Alimpiev et al. [1,2] using a continuously-tunable high-pressure CO_2 TEA laser exhibit several multiphoton resonances. The resonances may be identified with anharmonically-split levels of the lower ν_3 overtones of SF_6 calculated from the quartic anharmonic constants X_{33}, G_{33}, and T_{33} [3]. These constants have been determined from a detailed analysis of the $3\nu_3$ bands of SF_6 [4,5] recorded at Doppler-limited resolution [6]. These same parameters have also been obtained for SiF_4 from similar $3\nu_3$ data [7] and can be used to predict the multiphoton resonances for this molecule.

Given the anharmonic constants, one can predict the positions of the vibrational sublevels, or, equivalently, the Q-branch origins of the $n\nu_3$ ladder by diagonalizing the vibrational hamiltonian [3]

$$H_v = (n\omega_3^0 + n^2X_{33})\,\mathbf{1} + G_{33}J_3^2 + T_{33}(120)^{1/2}T^{404}\,. \quad (1)$$

Such calculations [4–7] are helpful for delineating possibly strong multiphoton resonances since the Q-branches tend to be the most compact features. In addition the rotational structure must be included in the multiple photon absorption since it can compensate for for laser detuning from the anharmonically-split vibrational sublevels. The rotational structure itself is greatly perturbed by Coriolis-type interactions within each $n\nu_3$ manifold causing rotational shifts and intensity sharing which may distort the position and shape of the many branches. Thus it is possible to have R-branch band heads and Q-branches anomalously degraded to higher frequencies. These distortions are particularly noticeable at high J since the Coriolis interactions are proportional to J. For SF_6 and SiF_4 at $T = 100$ K the peak of the rotational Boltzman distribution occurs at $J = 36$ and $J = 23$ respectively. Therefore it is necessary to include all of the interactions to properly simulate the important multiphoton resonances in these molecules.

Remarkably, it is found that the important $3\nu_3$ rotational constants for SF_6 and SiF_4 agree with the previously determined ν_3 fundamental constants [8–11] to within one percent. This indicates that neither the ν_3 fundamental nor the $3\nu_3$ second overtone is discernably perturbed by neighboring vibra-

[1] The portion of this work performed at the Los Alamos National Laboratory was supported by the U.S. Department of Energy.

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tional levels. Thus one can calculate the rovibrational levels of the low overtones of ν_3 for SF_6 and SiF_4 without considering Fermi or Coriolis interactions with other vibrational levels. The rovibrational hamiltonian [3] for the nth level of excitation of the ν_3 mode is given by

$$H_n = H_v + B_n J^2 - 2(B\zeta_3)^{(n)}(J \cdot l_3) + (5)^{1/2} Z_{3s} T^{220} + (120)^{1/2} Z_{3t} T^{224} \quad (2)$$

where the tensor operators $T^{K_1 K_2 K}$ are of rank K_1 in the vibrational angular momentum l, rank K_2 in the total angular-momentum J, and rank K in the rotor angular momentum R, evaluated in the basis $|J;R\rangle$ [4] according to the coupling rule

$$J - l = R \,. \quad (3)$$

The normal selection rules operative for an n-photon resonance to $n\nu_3$ from the ground state are

$$\Delta l \leqslant n \,, \quad \Delta J \leqslant n \,, \quad \Delta R = 0 \,. \quad (4)$$

The $\Delta R = 0$ selection rule will be violated due to mixing of the R states by the last two operators in eq. (2). Such normally forbidden transitions are included automatically in our calculations.

The accuracy of using eq. (2) with the constants derived from ν_3 and $3\nu_3$ to predict the rovibrational energies of $2\nu_3$ has been confirmed in the case of SF_6. Indeed, the calculated rovibrational levels of $2\nu_3$ for SF_6 were used to assign IR-IR double resonance $2\nu_2 \leftarrow \nu_3$ transitions excited with a tunable diode laser [12] or CO_2 laser [13] and also two-photon $2\nu_3 \leftarrow 0$ sub-Doppler transitions [14]. The calculated levels of $2\nu_3$ for SF_6 were accurate to within 0.01 cm^{-1}. A similar accuracy is expected for calculations of the $2\nu_3$ levels of SiF_4. Of course, the determination of the ν_3 and $3\nu_3$ rovibrational levels themselves is even more accurate (<0.001 cm^{-1}).

In fig. 1 we show the possible SF_6 rovibrational one-, two-, and three-photon resonances to ν_3, $2\nu_3$, and $3\nu_3$, respectively, which result from diagonalizing eq. (2) with the appropriate constants. Also shown above the multi-photon spectra are the possible normal isotope 10.6 μm CO_2 pump lines. The position of the Q-branch band origins given by eq. (1) for the vibrational sublevels, labeled by their octahedral symmetry, are also shown above each spectrum. The parity of the $n\nu_3$ vibrational sublevels is $(-1)^n$. The spec-

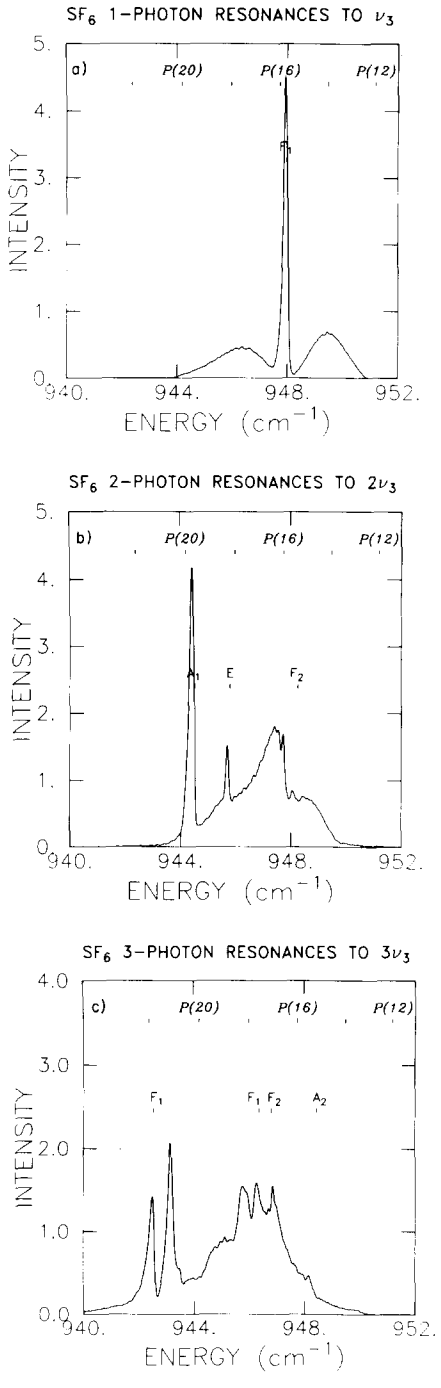

Fig. 1. a) One-photon b) two-photon and c) three-photon resonances to ν_3 $2\nu_3$ and $3\nu_3$ of SF_6 at 100 K with a 0.1 cm^{-1} FWHM Lorentzian profile for $J \leqslant 50$. Also shown are the positions of the vibrational band origins and the positions of the normal isotope 10.6 μm CO_2 lines.

tra of fig. 1 are calculated at $T = 100$ K for $J \leqslant 50$ with the transitions lorentzian broadened to 0.1 cm^{-1} FWHM to correspond to the linewidth of a CO_2 high pressure TEA laser and the expected power broadening. These spectra represent a compendium of the possible rovibrational transitions and include all important interactions within the $n\nu_3$ manifold.

The number of branches for an n-photon resonance to $n\nu_3$ is equal to the vibrational degeneracy. The intensity (absorbance) scale is normalized such that each branch has an integrated strength of one (cm^{-1}) before diagonalizing eq. (2); i.e., the total integrated intensity for ν_3, $2\nu_3$, and $3\nu_3$ will be 3, 6, and 10 in figs. 1a, 1b and 1c, respectively. Transitions strengths are moderated by the square of the eigenvectors after diagonalizing to include intensity borrowing between the sublevels. Note for example that the E vibration sublevel of $2\nu_3$ loses intensity due to the strong Coriolis interaction with the F_2 sublevel. Selection rules restrict the $2\nu_3$ A_1 sublevel transitions to the sharp Q branch. The Fermi and Coriolis interactions in $3\nu_3$ give rise to the sharp three-photon R-branch band head seen at 943.2 cm^{-1} exactly as observed in the $3\nu_3 \leftarrow 0$ spectrum [6].

The spectra shown in fig. 1 assume the laser intensity is sufficiently strong such that each rovibrational transition is significantly populated and do not include the pathway dependent effects of laser detuning from intermediate levels. Such a dynamical treatment which includes detunings is only possible by solving the dressed Schrodinger equation for the multilevel system where all rotational levels up to $n\nu_3$ are coupled by the laser field. Such calculations have been performed for SF_6 with all levels up to $3\nu_3$ but with rotational states limited to those appreciable populated at 10 K [15,16]. By limiting pathways to those with the least laser detuning, calculations at higher temperatures (more rotational states) can be performed [17]. No such calculations for SiF_4 have, as yet, been undertaken.

The spectra in fig. 1 also do not include the effects due to absorption further up the ν_3 ladder which certainly will occur at laser intensities where the multiphoton resonances are saturated. Indeed, it has been shown that the 2-photon resonances to the $2\nu_3$ A_1 level is also a good pathway up to perhaps as high as $10\nu_3$ [3]. This deficiency also will occur for dynamical calculations which treat the discrete levels of the ν_3 ladder.

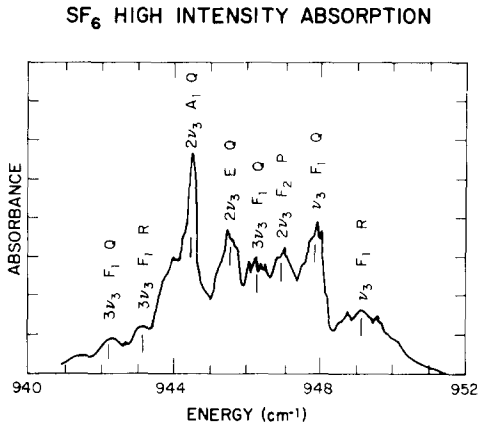

Fig. 2. Absorption of SF_6 with a ~7 MW/cm^2 tunable CO_2 laser source at 140 K with resolution 0.06 cm^{-1} under nearly collisionless conditions (0.3 Torr).

The purpose of the calculated spectra in fig. 1 is to identify the multiphoton resonances evident in the actual high intensity absorption spectrum of Alimpiev et al. [1] shown in fig. 2. This spectrum was taken with a high pressure continuously tunable CO_2 laser operating at 0.27 J/cm^2 with a 40 ns pulse and a laser bandwidth of ~0.06 cm^{-1}. The SF_6 gas was at a temperature of 140 K and a pressure of 0.3 Torr. From fig. 1 we may readily assign most of the features seen in fig. 2 to multiphoton resonances as shown. An assignment of a feature to a low order overtone would be expected to dominate higher order resonances at the same frequency.

Our assignments differ significantly from those made by Alimpiev et al. based on their own dissociation data [2]. Their assignments are made from the vibrational sublevel origins as shown above the spectra in fig. 1 and do not include the rotational analysis given here. We should note that the unassigned shoulder at 944.0 cm^{-1} is not observed in their dissociation data.

Fortunately, one does not need a detailed knowledge of the rotational structure to assign the sharp two-photon resonance to the $2\nu_3$ A_1 Q-branch since the A_1 mode is singly degenerate and relatively unperturbed. Note that all structure seen to lower frequencies than the $2\nu_3$ A_1 resonance must be higher order multiphoton resonances since neither fig. 1a nor 1b show structure there. In fact, the three-photon resonance to the $3\nu_3$ lower F_1 level is seen

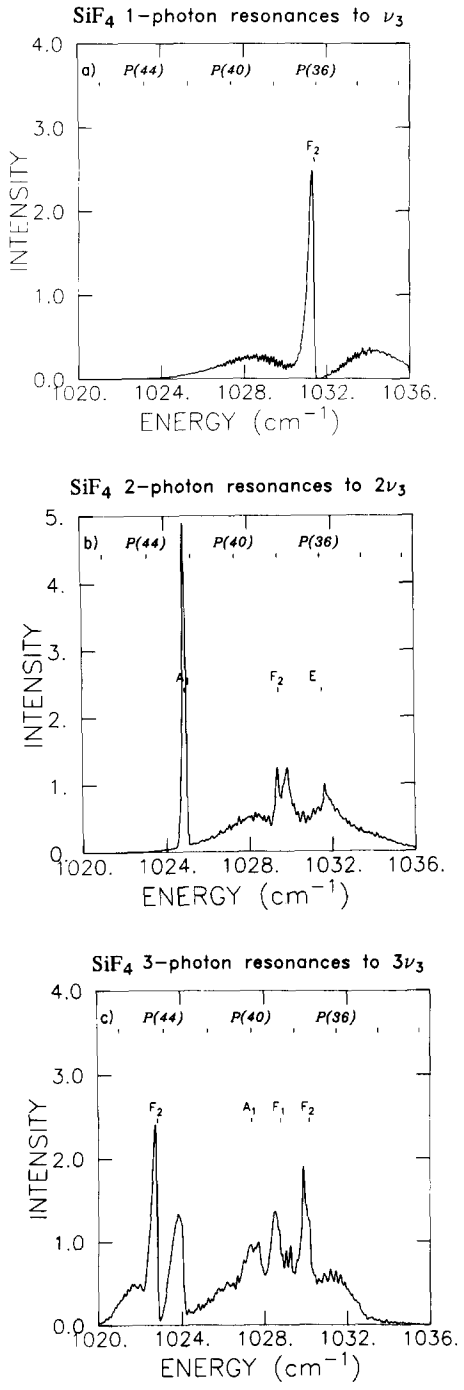

Fig. 3. a) One-photon b) two-photon and c) three-photon resonances to ν_3, $2\nu_3$ and $3\nu_3$ of SiF_4 under the same conditions as fig.1. Also shown are the positions of the vibrational band origins and the positions of the normal isotope 9.6 μm CO_2 lines.

at both 942.5 cm^{-1} and 943.2 cm^{-1} corresponding to Q- and R-branch transitions (that is, the total change in J is 0 and 1 respectively). These peaks correspond to those most apparent in the $3\nu_3$ high resolution spectra [4–6,18,19].

It is fortuitous that the CO_2 P(20) and P(22) lines are resonant with transitions to the $2\nu_3$ A_1 and the $3\nu_3$ lower F_1 levels. This means that SF_6 low intensity absorption should show quadratic and cubic intensity dependence when pumped with P(20) and P(22) lines respectively. An anomalous intensity dependence has indeed been observed using a P(20) CO_2 line [1]. We know of no relevant experiments with a P(22) pump line.

In fig. 3 we show the one-, two-, and three-photon rovibrational resonances for SiF_4. Also shown above the multiphoton spectra are the possible normal isotope 9.6 μm CO_2 pump lines. No absorption experiment using a tunable CO_2 laser has yet been performed for SiF_4. Fortunately, there are a few multiphoton resonances coincident with fixed frequency normal isotopic 9.4 μm CO_2 lines. The P(38) line is nearly resonant with $2\nu_3$ F_2 level while the P(40) line is resonance with the $3\nu_3$ A_1 level. However, the P(38) and P(40) lines also pump ν_3 P-branch lines with small detunings so that quadratic and cubic intensity dependence of the absorption will probably be obscured. Rather the P(38) and P(40) lines will excite stepwise without large intermediate detunings.

As in the case of SF_6, we surmise that the high intensity spectrum of SiF_4 would show a narrow absorption peak near 1025 cm^{-1} corresponding to a two-photon resonance to the $2\nu_3$ A_1 Q-branch. This frequency also represents the best pathway for dissociation based on our knowledge of ν_3 ladder [7]. We also expect to see three-photon resonances to the $3\nu_3$ lower F_2 Q- and R-branches at 1022.7 cm^{-1} and 1023.9 cm^{-1}. In general, as in the case of SF_6, we expect multiphoton resonances will dominate the high intensity SiF_4 spectrum.

References

[1] S.S. Alimpiev, N.V. Karlov, S.M. Nikiforov, A.M. Prokhorov, B.G. Sartakov, E.M. Khokhlov and A.L. Shtarkov, Opt. Commun. 31 (1979) 309.

[2] S.S. Alimpiev, N.V. Karlov, S.M. Nikiforov, B.G. Sartakov and A. L. Starkov, Laser Conference, New Orleans, 1981.

[3] K.T. Hecht, J. Mol. Spectrosc. 5 (1960) 355.
[4] C.W. Patterson, B.J. Krohn and A.S. Pine, J. Mol. Spectrosc. 88 (1981) 133.
[5] C.W. Patterson, B.J. Krohn and A.S. Pine, Opt. Lett. 6 (1981) 39.
[6] A.S. Pine and A.G. Robiette, J. Mol. Spectrosc. 80 (1980) 388.
[7] C.W. Patterson and A.S. Pine, J. Mol. Spectrosc., to be published.
[8] M. Loete, A. Clairon, A. Frichet, R.S. McDowell, H.W. Galbraith, J.-C. Hilico, J. Moret-Bailly and L. Henry, C.R. Acad. Sci. (Paris) 285B (1977) 175.
[9] Ch.J. Borde, M. Ouhayoun, A. Van Lerberghe, C. Saloman, S. Avrillier, C.D. Cantrell and J. Borde, Laser Spectroscopy IV, eds. H. Walther and K.W. Rothe (Springer-Verlag, New York, 1979) p. 142.
[10] C.W. Patterson, R.S. McDowell, N.G. Nereson, B.J. Krohn, J.S. Wells and F.R. Petersen, J. Mol. Spectrosc. 91 (1982) 416.
[11] R.S. McDowell, C.W. Patterson, N.G. Nereson, F.R. Petersen and J.S. Wells, Optics Lett. 6 (1981) 422; and erratum, ibid. 647.
[12] C.W. Patterson, R.S. McDowell, P. Moulton and A. Mooradian, Optics Lett. 6 (1981) 93.
[13] M. Dubs, D. Harradine, E. Schweiter, J.I. Steinfeld and C.W. Patterson, J. Chem. Phys., to be published.
[14] P. Herlemont, M. Lyszyk and J. Lemaire, Appl. Phys. 24 (1981) 369.
[15] D.P. Hodgkinson, A.J. Taylor and A.G. Robiette, J. Phys. B14 (1981) 1803.
[16] A.J. Taylor, D.P. Hodgkinson and A.G. Robiette, Optics Comm. 41 (1982) 320.
[17] D.P. Hodgkinson, A.J. Taylor, D.W. Wright and A.G. Robiette, private communication.
[18] H. Kildal, J. Chem. Phys. 67 (1977) 1287.
[19] J.R. Ackerhalt, H. Flicker, H.W. Galbraith, J. King and W.B. Person, J. Chem. Phys. 69 (1978) 1461.