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A new treatment of the $\upsilon_4 = 2$ excited state of the symmetric top molecule PF_3 around 693 cm^{-1}

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ABSTRACT

All experimental data of the $2\upsilon_4^0$ parallel and $2\upsilon_4^{-2}$ perpendicular components of the pyramidal molecule PF_3 have been refined using five equivalent *D*-, *Q*-, *QD*-, *L*-, *LD*-reduction forms of the effective rovibrational Hamiltonian recently developed for the $\upsilon_t(E) = 2$ vibrational state of a C_{3v} symmetric top molecule. The $\upsilon_4 = 2$ excited level of the PF_3 molecule has been treated with models taking into account ℓ- and *k*-intravibrational resonances. The body of data comprised 1171 IR lines of the $2\upsilon_4^0$ component, 249 energies of the $\upsilon_4 = 2^{-2}$ substate deduced from the $2\upsilon_4^{-2} - \upsilon_4^{-1}$ hot band and 5 reported MW data. The standard deviations of the fits are practically similar for the reductions applied and close to the quality of measurements. The unitary equivalence of the tested relations between the derived parameters was satisfactorily fulfilled.

1. Introduction

Phosphorus trifluoride PF_3, a ligand in metal complexes of chemistry interest, is an oblate symmetric top molecule belonging to C_{3v} point group. Therefore, it has four normal modes of vibration: two totally symmetric, υ_1 and υ_2, and two doubly degenerate, υ_3 and υ_4.

Quite recently, we studied by Fourier transform infrared (FTIR) spectroscopy the υ_2 [1] and υ_4 [2] fundamental bands. We determined an accurate rotational ground state (GS) C_0 value, 0.159970436 (69) cm^{-1}, which was used to derive an improved GS structure of PF_3, r_0(P-F) = 1.56324405 (11) Å and $\measuredangle$(FPF) = 97.752232 (29)°. The $\upsilon_2 = 1$ state was treated using a classical model. However, the degenerate vibrational level $\upsilon_4 = 1$ was treated by applying the theory of reduction of the effective rovibrational Hamiltonian H_{vr}.

The present work extends our investigations on the vibrationally excited states of fluoride molecules, phosphorus trifluoride PF_3 [1–9], and nitrogen trifluoride NF_3 [10–14]. The objective is to test, for the $\upsilon_4 = 2$ vibrational state of PF_3 around 693 cm^{-1}, the unitary equivalence of parameter sets obtained from different reduction forms of H_{vr}.

It has been demonstrated, for the $\upsilon_t = 1$ and $\upsilon_t = 2$ excited states of C_{3v} symmetric top molecules, that the molecular parameters of the effective rovibrational Hamiltonian cannot all be determined independently from the fitting of the experimental data, because they are strongly correlated. The number of parameters has to be reduced through a unitary transformation called reduction [15–21]. Many studies were performed [22–26] using this approach. The obtained results demonstrated that the procedure of reduction is an appropriate solution for the indeterminacy problems. Thus, we successfully applied reduction methods to the $\upsilon_3 = 1$ (E, $\upsilon_0 = 907.5413$ cm^{-1}) [10], $\upsilon_4 = 2$ (A_1, $\upsilon_0 = 983.7017$ cm^{-1}; E, $\upsilon_0 = 986.6223$ cm^{-1}) [11], $\upsilon_1 = \upsilon_3 = 1$ (E, $\upsilon_0 = 1931.5775$ cm^{-1}), and $\upsilon_3 = 2$ (A_1, $\upsilon_0 = 1803.1302$ cm^{-1}; E, $\upsilon_0 = 1810.4239$ cm^{-1}) [12] excited states of the nitrogen trifluoride $^{14}NF_3$. We also applied it more recently to the $\upsilon_4 = 1$ (E, $\upsilon_0 = 347.0861$ cm^{-1}) degenerated state [2] of the phosphorus trifluoride PF_3.

2. Theory

The diagonal and off-diagonal matrix elements of the Hamiltonian operator H_{vr} that were considered for the ground and $\upsilon_4 = 2$ states of PF_3, which include contributions of higher order as well as *K* and *J* dependences of the interaction parameters, were taken as:

– The ground state energy:

$$E_0(J,K) = (C_0 - B_0)K^2 + B_0J(J+1) - D_J^0J^2(J+1)2 - D_{JK}^0J(J+1)K^2 - D_K^0K^4 + H_{JJ}^0J^3(J+1)^3 + H_{JK}^0J^2(J+1)^2K^2 + H_{kJ}^0J(J+1)K^4 + H_{KK}^0K^6$$

where $K = |k|$.

– The excited state energy:

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$$E(v,\ell,J,K) = v_0 + (C-B)K^2 + BJ(J+1) - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4 + H_{JJ}J^3(J+1)^3 + H_{JKJ}J^2(J+1)^2K^2 + H_{KJ}J(J+1)K^4 + H_{KK}K^6 + [-2C\zeta + \eta_J J(J+1) + \eta_K K^2 + \eta_{JJ}J^2(J+1)^2 + \eta_{JK}J(J+1)K^2 + \eta_{KK}K^4]k\ell$$

where $\ell = 0, \pm 2$.

– The $\ell(2, 2)$ interaction (q resonance) between $2v_4^0$ and $2v_4^{-2}$ components, employing the phase convention of Cartwright and Mills [27]:

$$< v,\ell,J,kH_{vr}/hcv,\ell \pm 2,J,k \pm 2 > = -1/4q + q_J J(J+1) + q_K[k^2 + (k \pm 2)^2] + q_{JJ}J^2(J+1)^2 + q_{JK}J(J+1)[k^2 + (k \pm 2)^2]x[(v \pm \ell + 2) \times (v \mp \ell))]^{1/2}F \pm (J,k)F \pm (J,k \pm 1)$$

with $F \pm (J,k) = [J(J+1) - k(k \pm 1)]^{1/2}$.

– The $\ell(2, -1)$ interaction (r resonance) between $2v_4^0$ and $2v_4^{-2}$ components:

$$< v,\ell,J,kH_{vr}/hcv,\ell \mp 2,J,k \pm 1 > = r(2k \pm 1)x[(v \pm \ell + 2)(v \mp \ell)]^{1/2}F \pm (J,k)$$

– The $k(0, 3)$ interaction (ℓ-dependent d resonance):

$$< v,\ell = \pm 2,J,kH_{vr}/hcv,\ell = \pm 2,J,k \pm 3 > = \ell dF \pm (J,k)F \pm (J,k \pm 1)F \pm (J,k \pm 2)$$

– The $k(0, 3)$ interaction (ℓ-independent ε resonance):

$$< v,J,kH_{vr}/hcv,J,k \pm 3 > = \varepsilon(2k \pm 3)F \pm (J,k)F \pm (J,k \pm 1)F \pm (J,k \pm 2)$$

According to the theory of equivalent reductions, and in order to prevent correlations in the fitting experimental data, some of the molecular parameters have to be constrained. One of the off-diagonal parameters accounting for $\Delta(k - \ell) \neq 0$ interaction can be refined while the others are fixed, usually to zero value.

In the case of an isolated $v_t = 2$ state of a symmetric top, five equivalent *D*-, *Q*-, *QD*-, *L*-, and *LD*-reduction schemes were proposed [15–19].

– In the *D*-reduction, the d and ε parameters of the (0, 3) k-type interaction are constrained to zero, while the r parameter of the (2, −1) ℓ-type resonance is refined.
– In the *Q*-reduction, the r and ε parameters are fixed to zero.
– In the *QD*-reduction, the ε parameter is refined.
– In the *L*- and *LD*-reduction, the constraints concern the two interaction constants ε and d respectively.

Furthermore, the condition $r_K = 0$ and $q_K = 0$, or $\eta_{JJ} = 0$, or $\eta_{JK} = 0$, or $\eta_{KK} = 0$ has to be imposed in all reductions in order to avoid collinearity problems [16,18].

3. Results and discussion

The set of the experimental data of the $2v_4$ overtone band of PF_3 used in this work is the same as in our previous study of the $v_4 = 2$ state of PF_3 [7]. The body of data comprised 1171 non-zero-weighted (NZW) infrared lines of the $2v_4^0$ parallel component, 249 NZW energies of the $v_4 = 2^{-2}$ substate deduced from the observed $2v_4^{-2} - v_4^{-1}$ hot band and five reported microwave data [30].

The fit calculations were carried out with the nonlinear least-squares program SIMFIT [28], according to the same reduction schemes of the rovibrational Hamiltonian already performed for the $v_4 = 2$ excited level of NF_3 [11]. A unit weight was ascribed to each pure IR line, while 0.1, 0.01 and 0.001 weights were given to the IR observed wavenumbers that differed from the corresponding calculated values by more than 2×10^{-3} cm^{-1}. A weight of 100 was assigned to the 5 MW transitions. The GS constants were fixed to the values of Table 1. All experimental data of the $2v_4$ overtone band of PF_3 were fitted with the five reduction forms of the rovibrational Hamiltonian H_{rv} proposed by Sarka and Harder [18]. According to the theory of reduction of H_{rv}, the q_K parameter of the $\ell(2, 2)$ interaction was refined, and the η_{JK} parameter was fixed to zero. The q_{JJ} and q_{JK} parameters of the q resonance could not be statistically determined and were constrained to the $v_4 = 1$ state values [2]. For the same reason, we fixed the η_{JJ} and η_{KK} terms. The results obtained in different reductions for the $v_4 = 2$ state of PF_3 are given in Table 2.

As can be seen in this Table, all parameters appear at the correct order of magnitude. The standard deviations of the fits are practically similar for the five reductions applied, and close to the quality of measurements.

The C, B rotational constants, the $C\zeta$ term of the Coriolis interaction, the centrifugal distortion constants, and the q coupling term should not be affected by the unitary transformation. Table 2 shows that these parameters have compatible values in the five forms of reduction.

The unitary equivalence of the obtained parameter sets corresponding to the *D*-, *Q*-, *QD*-, *L*-, and *LD*-reductions can be checked with expressions deduced from the theory reduction of H_{rv}. The relations that we tested are given in Table 3.

It is worth noting that all six sets of expressions are satisfactorily fulfilled; with some reservations concerning Eqs. (1) and (4). The fulfillment is particularly appreciable for the Eqs. (2) and (5). This agreement confirms the unitary equivalence of reductions *D*, *Q*, *QD*, *L* and *LD* for fitting the $2v_4$ overtone band of PF_3. Because of a lack information about the $2v_4^{+2}$ side of PF_3, the values obtained for the r coupling term in *D*-, *L*- and *LD*-reductions are quite different from the $v_4 = 1$ state [2] and damage the validity.

There are a few more equations which may be used to test the equivalence of parameters in different reductions applied to the $v_4 = 2$ state of PF_3. However, they involve in particular parameters and their differences which could not be determined with sufficiently high significance to be used for comparison, and were therefore omitted.

In conclusion, the consistency obtained between the parameters, in the reductions checked in this study, strengthens the

Table 1
Ground state constants (cm^{-1}) of PF_3.

Parameter	Value	Ref.
C_0	0.159970436 (69)	[2]
B_0	0.2608469623 (36)	[29]
$D_J^0 \times 10^7$	2.619095 (46)	[29]
$D_{JK}^0 \times 10^7$	−3.92547 (18)	[29]
$D_K^0 \times 10^7$	1.73[a]	[30]
$H_{JJ}^0 \times 10^{13}$	5.421 (26)	[29]
$H_{JK}^0 \times 10^{12}$	−2.330 (23)	[29]
$H_{kJ}^0 \times 10^{12}$	3.102 (46)	[29]
$H_{kk}^0 \times 10^{12}$	0[b]	–

[a] From harmonic force field calculations, uncertainty not given.
[b] Fixed to zero because unknown.