Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Spectroscopy 239 (2006) 160–173
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

Rotation–vibration energy level clustering in the $\widetilde{X}^2B_1$ ground electronic state of PH_2

S.N. Yurchenko [a,*], W. Thiel [a], Per Jensen [b], P.R. Bunker [c]

[a] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany*
[b] *FB C—Mathematik und Naturwissenschaften, Fachgruppe Chemie, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany*
[c] *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6*

Received 12 May 2006; in revised form 15 June 2006
Available online 15 July 2006

Abstract

We use previously determined potential energy surfaces for the Renner-coupled $\widetilde{X}^2B_1$ and $\widetilde{A}^2A_1$ electronic states of the phosphino (PH_2) free radical in a calculation of the energies and wavefunctions of highly excited rotational and vibrational energy levels of the $\widetilde{X}$ state. We show how spin–orbit coupling, the Renner effect, rotational excitation, and vibrational excitation affect the clustered energy level patterns that occur. We consider both 4-fold rotational energy level clustering caused by centrifugal distortion, and vibrational energy level pairing caused by local mode behaviour. We also calculate *ab initio* dipole moment surfaces for the $\widetilde{X}$ and $\widetilde{A}$ states, and the $\widetilde{X}$–$\widetilde{A}$ transition moment surface, in order to obtain spectral intensities.

Keywords: Phosphino; Renner; Local mode; Ab initio; Dipole moment; Intensity

1. Introduction

Analytical expressions for the potential energy surfaces of the $\widetilde{X}^2B_1$ and $\widetilde{A}^2A_1$ electronic states of the phosphino (PH_2) free radical were obtained in a recent dispersed fluorescence and *ab initio* investigation [1]. The details of how these potentials were obtained, and a discussion of previous experimental and theoretical studies on PH_2, are given in Ref. [1]. Using these potentials, the $\widetilde{X}$ state has a $\mathbf{C}_{2v}$ equilibrium structure with bond length $r_e = 1.418$ Å and bond angle $\alpha_e = 91.7°$; the $\widetilde{A}$ state has a $\mathbf{C}_{2v}$ equilibrium structure with $r_e = 1.394$ Å and $\alpha_e = 121.7°$; the barrier to linearity is 24 911.8 cm^{-1} in the $\widetilde{X}$ state and 6 686.3 cm^{-1} in the $\widetilde{A}$ state; and $T_e(\widetilde{A}) = 18225.5\,\mathrm{cm}^{-1}$. Particular interest attaches to these two states since they become degenerate as a $^2\Pi_u$ state at linearity (see Fig. 1). As a result, they are subject to the Renner effect described, for example, in Ref. [2] and in chapters 15 and 16 of Ref. [3].

In the present paper, we use the potential energy surfaces from Ref. [1] in the computer program RENNER [4–6] to calculate rotational energies for $\widetilde{X}$-state PH_2 at high angular momentum (when the rovibronic angular momentum quantum number $N \simeq 30$) in order to determine the extent of the rotational energy level clustering. Previous studies of rotational energy level clustering in triatomic molecules have concerned singlet states that are not subject to the Renner effect (see, for example, Refs. [7–10] and the references therein). We use PH_2 as an example in order to study how spin–orbit coupling and the Renner effect alter the clustering in the $\widetilde{X}$ state. We also consider, for the $\widetilde{X}$ state, the effect on the cluster formation when the stretching and bending vibrational modes are excited, and investigate the local mode character [11] of excited stretching states. For the purpose of predicting spectral intensities we calculate *ab initio* the dipole moment surfaces of the $\widetilde{X}$ and $\widetilde{A}$ states, and the $\widetilde{X}$–$\widetilde{A}$ transition moment surface.

In low angular momentum states the rotational energy level pattern for an XH_2 molecule is essentially that of a rigid asymmetric top molecule and, in particular, the four highest energies for a given value of N form two

---

[*] Corresponding author. Fax: +49 208 306 2996.
E-mail address: yurchenko@mpi-muelheim.mpg.de (S.N. Yurchenko).

0022-2852/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2006.07.002

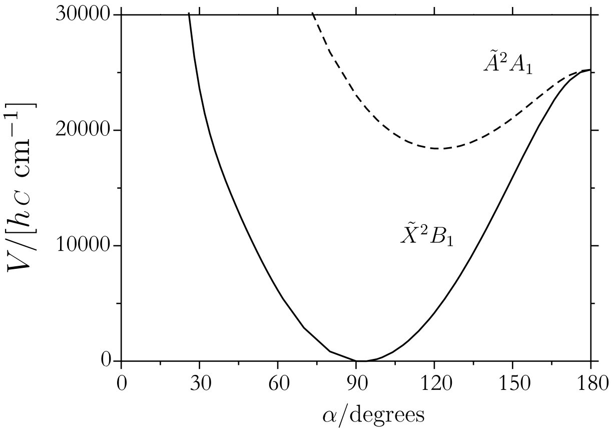

Fig. 1. The $\widetilde{X}$ and $\widetilde{A}$ potential energy curves of PH_2 as a function of the bond angle α (from Ref. [1]). The bond lengths are fixed at 1.4 Å.

K-doublets whose energy separation increases with *N*. However, at high *N* these two doublets can move close together to form a 4-fold cluster (see, for example, Fig. 2 of Ref. [8]). XH_2 molecules that have a heavy central atom X, little intermode coupling, and a bond angle close to 90°, are ideal cases for such 4-fold rotational energy level clusters to form, and these same three requirements also lead to local mode behaviour for the stretching vibrational states. Thus, PH_2 in its $\widetilde{X}$ state is a good candidate for studying both phenomena. Classically, the formation of 4-fold clusters for XH_2 molecules corresponds to the possibility being realized in high angular momentum states for there to be stable right- and left-handed rotation about each of two equivalent rotational axes, and in the ideal case these axes are aligned with the XH bonds as shown in Fig. 2. The subject of 4-fold energy level clustering in XH_2 molecules is reviewed in Ref. [10], and the interrelation with local mode vibration is described for such molecules in Ref. [11].

Semiclassical theory [7] predicts that in the ideal case 4-fold rotational energy level clustering will begin to form when *N* exceeds the critical value N_{cr} given by

$$N_{\mathrm{cr}} = \frac{v_2}{4A}\sqrt{\frac{A-B}{C}}, \tag{1}$$

where v_2 is the wavenumber of the bending mode, and *A*, *B*, and *C* are the rotational constants in cm^{-1}. For the $\widetilde{X}$ state of PH_2 using the experimental values [12] of v_2, *A*, *B*, and *C*, we have $N_{\mathrm{cr}} \simeq 15$. Divergence from the ideal case arises because of the finite mass of the central atom, deviation of the bond angle from 90°, and from the presence of intermode coupling; these effects shift the cluster formation to higher *N* values. The present paper evaluates further effects on the cluster formation that arise from the presence of electronic angular momentum and vibrational excitation for the $\widetilde{X}$ state of PH_2. We do not consider the possibility of rotational energy level clustering in the $\widetilde{A}$ state since its equilibrium bond angle is far from 90°.

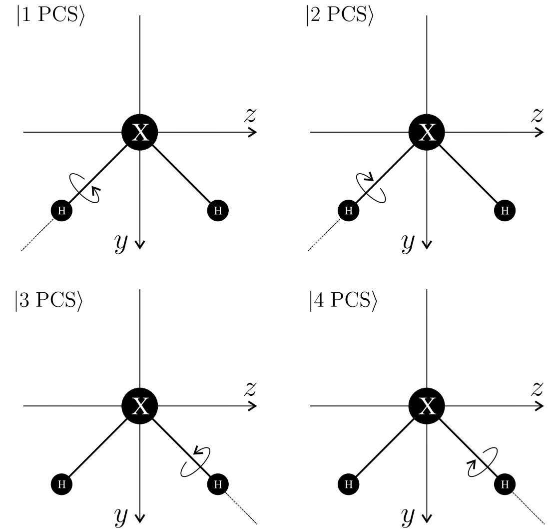

Fig. 2. The four localized *Primitive Cluster States* occurring at highest energy in an *N* multiplet for an ideal XH_2 molecule at high angular momentum.

2. The potential energy and dipole moment surfaces

The lower ($\widetilde{X}$) and upper ($\widetilde{A}$) potential energy surfaces, $V_-(\Delta r_{12},\Delta r_{32},\bar{\rho})$ and $V_+(\Delta r_{12},\Delta r_{32},\bar{\rho})$, respectively, are written

$$\begin{aligned} V_\pm(\Delta r_{12},\Delta r_{32},\bar{\rho}) &= V_0^{(\pm)}(\bar{\rho}) + \sum_j F_j^{(\pm)}(\bar{\rho})y_j + \sum_{j\leqslant k} F_{jk}^{(\pm)}(\bar{\rho})y_jy_k \\ &\quad + \sum_{j\leqslant k\leqslant m} F_{jkm}^{(\pm)}(\bar{\rho})y_jy_ky_m + \sum_{j\leqslant k\leqslant m\leqslant n} F_{jkmn}^{(\pm)}(\bar{\rho})y_jy_ky_my_n, \end{aligned} \tag{2}$$

with

$$y_j = 1 - \exp(-a_1\Delta r_{j2}), \tag{3}$$

$$F_{jk\dots}^{(\pm)}(\bar{\rho}) = f_{jk\dots}^{(0)} + \sum_{i=1}^{N} f_{jk\dots}^{(i,\pm)}(1-\cos\bar{\rho})^i, \tag{4}$$

and

$$V_0^{(\pm)}(\bar{\rho}) = \sum_{i=1}^{8} f_0^{(i,\pm)}(1-\cos\bar{\rho})^i. \tag{5}$$

In Eq. (2), $\bar{\rho}$ is the instantaneous value of the bond angle supplement (see Figs. 15–14 of Ref. [13]), and $\Delta r_{j2} = r_{j2} - r^{(\mathrm{ref})}$, where the r_{j2} are the instantaneous P–H_j bond lengths and $r^{(\mathrm{ref})}$ is the reference value of these quantities, which is taken as the optimum bond lengths at linearity; the indices *j*, *k*, *m*, and *n* can each be 1 or 3. In Eq. (3), a_1 is a molecular parameter. In Eq. (4), the parameters $f_{jk\dots}^{(0)}$ are common for the two potential energy surfaces and this ensures that the functions are degenerate at linearity when $\bar{\rho} = 0$; the function $F_j^{(\pm)}(\bar{\rho})$ has $N = 4$, $F_{jk}^{(\pm)}(\bar{\rho})$ has $N = 3$, $F_{jkl}^{(\pm)}(\bar{\rho})$ has $N = 2$, and $F_{jklm}^{(\pm)}(\bar{\rho})$ has $N = 1$. The adjustable parameters $f_{\dots}^{()}$ in V_- and V_+ are constrained to ensure that V_- and V_+ are totally symmetric under the interchange of Δr_{12} and Δr_{32} which they must be for a symmetrical molecule like PH_2.