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Rotational energy cluster formation in XY_3 molecules: Excited vibrational states of BiH_3 and SbH_3

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Abstract

Previous theoretical work on energy cluster formation at high rotational excitation in the vibrational ground state of PH_3 [S.N. Yurchenko, W. Thiel, S. Patchkovskii, P. Jensen, Phys. Chem. Chem. Phys. 7 (2005) 573] is extended to BiH_3 and SbH_3. By means of variational calculations of the rotation–vibration energies based on *ab initio* potential energy surfaces, we analyze the rotational energy clustering of BiH_3 and SbH_3 at $J \leqslant 70$ for a number of vibrational states. We show that BiH_3 and SbH_3, with their pronounced local mode behaviour, exhibit cluster formation already at moderate rotational excitation. In addition, owing to its quasi-spherical-top character, BiH_3 undergoes an imperfect bifurcation at high J. This gives rise to an energy cluster type not present in PH_3 and SbH_3. We present a semi-classical approach to the construction of the rotational energy surfaces for vibrationally excited states.

Keywords: Energy clusters; Rotational energy; Excited vibrational states; Bifurcations; Local mode

1. Introduction

We have recently demonstrated by theoretical calculation [1] that in the vibrational ground state of PH_3, the highly excited rotational states form near-degenerate energy clusters. We have also computed the line strengths for transitions involving these cluster states [2]. In the present work, we study theoretically the energy-cluster formation in BiH_3 and SbH_3. In these molecules, in particular in BiH_3, the energy clusters form at lower rotational excitation than in PH_3 and, in consequence, the theoretical calculation of the cluster energies is computationally less demanding. Because of this, we have been able to extend the study of the cluster phenomenon to the vibrationally excited states of BiH_3 and SbH_3.

The formation of rotational energy clusters in a molecule provides a good example of how a system, which is completely described by quantum mechanics at low energy, approaches the classical limit, at least for the rotational motion, with increasing excitation. The parameter governing the transition is the angular momentum quantum number J (see, for example, Ref. [3]). By studying the rotational motion of the molecule from $J = 0$ to $J \gg 1$, we can follow the continuous change from an entirely quantum mechanical system to one where the rotational motion is classical. This transition connects two modelling paradigms: At the low-energy, quantum-mechanical limit, the molecular rotation is described by a simple rigid-rotor model, whereas at very high energy, another simple model, involving classical trajectories, is applicable. Between the two limits there is an intermediate region with a dense and disordered energy structure which is difficult to interpret.

In highly excited rotational states, we typically find that characteristic ‘stable’ axes of rotation emerge, about which the molecule prefers to rotate. This type of rotation tends to simplify the rotational energy level pattern since, when several symmetrically equivalent stable axes are present, the rotational energy levels form clusters, that is, groups

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of quasi-degenerate energy levels. Dorney and Watson [4] were the first to realize this; they explained the energy cluster formation in spherical top molecules in terms of classical rotation about symmetrically equivalent axes. Subsequently, Harter and co-workers (see, for example, Refs. [5,6]) have developed extensive classical models for the qualitative description of rotational-energy cluster formation in XY_N molecules. They introduced the now well-known concept of a *rotational energy surface* (RES), defined as the classical (or semi-classical) rotational energy of a molecule obtained as a function of the direction (relative to the molecule) of the classical angular momentum vector, which is taken to have a length of $|\mathbf{J}| = \sqrt{J(J+1)}\hbar$. The topology of the RES (in particular its stationary points) defines the patterns of the rotational energy levels. Pavlichenkov and Zhilinskií [7] illustrated how the bifurcation of stationary points on the RES affects the formation of rotational energy clusters. The role of symmetry in the cluster formation process has been also studied in great detail (see, for example, [8]).

In addition to the classical studies there have been many quantitative, quantum-mechanical studies of the rotational cluster formation (see, for example, the reviews [9,10]). This work was concerned with dihydrides H_2X and, to a lesser extent, with methane-type spherical top molecules XY_4. As mentioned above we have recently extended this work to XY_3 molecules in that we have shown by variational, quantum-mechanical calculation that rotational energy clusters form in the vibrational ground state of PH_3. We have characterized two basic types of rotational clusters for PH_3: Two- and sixfold clusters. The twofold clusters are associated with classical rotation about an axis close to the C_3 rotational symmetry axis for a PH_3 molecule at equilibrium; this axis is found to be stable at any value of J. The sixfold energy clusters can be understood as resulting from (clockwise or anti-clockwise) rotation about three symmetrically equivalent axes A (see Fig. 1). These axes lie in planes close to the three planes of reflection of a PH_3 molecule at equilibrium. As J increases, each axis approaches one of the P–H bonds. Thus, in a somewhat simplistic picture, we can think of the rotation in the cluster states at $J \to \infty$ as taking place about the three P–H bonds in PH_3. In this situation, the P–H localized rotation is naturally orthogonal to any other degree of freedom and, thus, reaches the highest degree of separation from these. We know that separations of this kind between vibrational degrees of freedom cause local-mode behaviour [10,11] and it was discussed for triatomic dihydrides H_2X in Ref. [10] how the local mode behaviour is intimately related to the phenomenon of energy clustering. An H_2X molecule whose vibration is well described by a local-mode model will have rotational energy clusters at relatively low rotational excitation. We expect that analogously, XH_3 molecules with pronounced local-mode behaviour will exhibit sixfold energy clusters at relatively low rotational excitation. The PH_3 molecule, however, whose cluster formation has been studied in Refs. [1,2], is far from being an ideal local-mode molecule, and therefore it is not an ideal case for studying cluster formation. The ultimate limit of complete mode separation, achieved by rotational excitation, is physically inaccessible for PH_3: Before it is reached, centrifugal distortion breaks the P–H bonds [1].

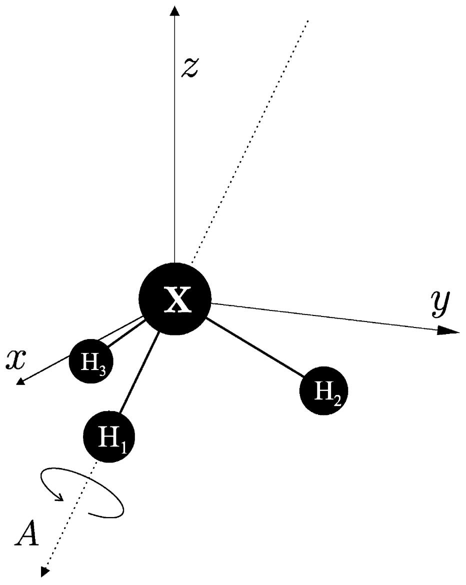

Fig. 1. The labeling of the nuclei chosen for XH_3, the molecule-fixed z axis, and the localization axis A (see text).

In our search for 'ideal' local-mode XY_3 molecules with 'perfect' energy clustering effects, we consider here the molecules BiH_3 and SbH_3. BiH_3 is a typical local-mode molecule [12] with a heavy central Bi atom bound to three much lighter H atoms. It has small intermode coupling and bond angles very close to 90°. The large ratio of the Bi mass to the proton mass, the small intermode coupling, and the near-90° bond angles are all conducive to local mode behaviour [10]. The fact that the Bi–H bonds are almost orthogonal makes them ideally oriented for stable rotations. As mentioned above, for BiH_3 and SbH_3 it is viable to compute highly excited rotational energies in excited vibrational states, and so we can study the cluster formation in these states. Local-mode theory predicts that stretching excitation accelerates the stabilization of the rotational axes [10] and, therefore, it makes the rotational energy clusters form at lower J values than in the vibrational ground state. We show in the present work that the BiH_3 and SbH_3 cluster formation indeed is 'faster' in this sense than that of PH_3. It is even more interesting that the rotational energy level patterns of BiH_3 exhibit special cluster features not found in the case of the less pronounced local-mode molecule PH_3. An important reason for the differences in cluster formation between PH_3 and BiH_3 is that BiH_3 is an almost perfect, accidental spherical top [13]. In order to see how this affects the rotational cluster formation, we compare the results for BiH_3 with those obtained for SbH_3. SbH_3 has local-mode properties very similar to those of BiH_3, but it has a less pronounced spherical top character.