

Molecular Quantum States at Dissociation

Highly Excited Rotational Dynamics of H_3^+

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I. INTRODUCTION

Considerable interest has been shown in highly rotationally excited states of molecules. This has been motivated by new theoretical and experimental investigations of the predissociation spectrum of H_3^+ [1], critical phenomena in water-like molecules [2,3], variational calculations of CF_4 [4,5] and the dissociation and rearrangements of argon clusters [6,7], to name just a few. In each of these areas an analysis of the classical system has proved to be very useful since it provides physical insights into the rotational dynamics of the molecular system, something which is usually lacking in variational calculations of molecular spectra. The classical and quantum approaches to the same molecule should therefore be viewed as complementary.

The results described here have been developed from earlier works by Zhilinskii, Pavlichenkov and Kozin [2,8] and Roberts, Sousa Dias and Montaldi [9] on *relative equilibria* of molecules. These are classical trajectories corresponding to steady rotations of molecules about stationary axes during which the shapes of the molecules remain constant. The main idea is to take advantage of the fact that the total angular momentum \mathbf{J} is an integral of motion and the Hamiltonian can be regarded as being parameterised by $J = |\mathbf{J}|$. This approach resembles in many respects the works of Lohr on argon clusters [7]. It also lies behind the general formalism of Jellinek and Li [10] describing the separation of rotational energy and in particular their analysis of \mathbf{J} -dependent normal vibrational modes. Related concepts appear in the work of Miller and Wales [11], who classify relative equilibria (there called stationary points) by their Hessian indices, and in the analysis of angular momentum barriers to dissociation in multi-atomic molecules by Pollak [12] and Chambers and Child [13]. A unifying theme of all these methods is their use of the so-called effective potential function $V_{\text{eff}} = V(\mathbf{q}) + 1/2 \mathbf{J} \mathbf{I}^{-1} \mathbf{J}$ which incorporates both the potential and rotational energy and drives the molecular dynamics in the vicinity of the relative equilibria.

The present work gives a detailed description of *all* relative equilibria of the H_3^+ ion and how they change as the total angular momentum increases, assuming an isolated ground electronic state. We are aware of the fact that at high energies the influence of other electronic states must be taken

into account [14] and our analysis at energies close to dissociation should only be considered as giving a rough idea of what might happen. It is a major problem to extend the classical analysis given here to two-fold potential energy surfaces or to points of energy surface switching. However we were surprised to find that the global maps of relative equilibria of H_3^+ as functions of J are qualitatively similar for a model pairwise potential based on just one Morse function and for the recent very accurate potential due to Dinelli, Polyansky and Tennyson [15]. All the results below are given for this latter potential. Full details will appear in [16].

II. THE PROCEDURE

An appropriate Hamiltonian for non-linear configurations of a molecule is given in [8] and for dynamics near a linear reference configuration in [16]. In both cases the Hamiltonian looks like

$$H = \frac{1}{2} \mathbf{J} \boldsymbol{\mu} \mathbf{J} - \mathbf{J} \mathbf{C} \mathbf{p} + \frac{1}{2} \mathbf{p} \mathbf{B} \mathbf{p} + V \quad (1)$$

where \mathbf{q} is an appropriate vector describing the shape of the molecule, \mathbf{p} is the corresponding vector of momenta, $\boldsymbol{\mu}$ is an inverted modified inertia tensor, \mathbf{C} is a matrix describing the Coriolis interaction, \mathbf{B} is the vibrational kinetic energy matrix, and V is the potential energy function. The matrices $\boldsymbol{\mu}$, \mathbf{C} and \mathbf{B} and the function V all depend on \mathbf{q} . For triatomic molecules the vectors \mathbf{q} and \mathbf{p} are three dimensional for the non-linear Hamiltonian and four dimensional for the linear Hamiltonian. In the latter case an extra symmetry and conserved constraint are used to recover the correct dimension.

The equations of motion are straightforward for coordinates and momenta:

$$\dot{q}_n = \partial H / \partial p_n; \quad \dot{p}_n = -\partial H / \partial q_n \quad (2)$$

while the equations for the angular momentum \mathbf{J} make use of Poisson brackets:

$$\dot{J}_\alpha = \{J_\alpha, H\}. \quad (3)$$

The relative equilibria are the points in phase space where all time derivatives are zero. For fixed \mathbf{J} the equilibrium solutions of Eqs. (2) are precisely the solutions of $\partial V_{\text{eff}} / \partial q_n = 0$, i.e. the stationary points of the effective potential. For the particular case of triatomic molecules, setting the right hand side of Eq. (3) to zero shows that the direction of \mathbf{J} must be either in, or perpendicular to, the molecular plane. This set of equations for the relative equilibria can be obtained in an analytic form and then

solved numerically using MATHEMATICA and the total energies of the relative equilibria plotted as functions of J . An example is given in Fig. 1.

The next step is to consider small oscillations around each of the relative equilibria. The normal modes and their frequencies are found by diagonalising the linearised equations of motion. In general the frequencies are distinct and the normal modes are mixtures of the internal ‘shape oscillations’ and precessional motion. If all the frequencies are real the relative equilibrium is said to be linearly stable and the classical phase space nearby is dominated by bound trajectories. If the relative equilibrium is a minimum of the Hamiltonian, and so its Hessian matrix has no negative eigenvalues, then it is automatically linearly stable. However it is important to note that a relative equilibrium may also be linearly stable if its Hessian matrix has any even number of negative eigenvalues. An example is provided by the maximum energy relative equilibrium of an asymmetric rotor.

III. RESULTS

A classical picture of the rotational dynamics of the H_3^+ ion and its isotopic modifications up to and above the dissociation limit has been obtained by a global study of their relative equilibria and stabilities. Several remarkable phenomena were observed. For example H_2D^+ exhibits critical phenomena similar to those predicted for water [2] and observed in H_2Se [3]. However, unlike for water-type molecules, the equilibrium bending angle is less than 90° and there is not only a bifurcation of the in-plane stable precession axis but also of the in-plane unstable axis.

It was confirmed that for H_3^+ , H_2D^+ and D_2H^+ the lowest energy relative equilibrium has linear geometry at sufficiently high values of the total angular momentum J [12,13]. Furthermore the series of bifurcations and changes of stability that accompany the transfer of stability from the rotating equilateral triangle configuration (in the H_3^+ case) to a linear configuration have been computed (see Fig. 1 for H_3^+).

Interestingly, the rotating equilateral triangle remains linearly stable for a large range of angular momentum values beyond the point where it ceases to be a minimum of the energy function. In this range, the Hessian matrix of the Hamiltonian has two negative eigenvalues but the frequencies remain real. In a quantum model this should correspond to a mode with an energy pattern which decreases in energy rather than increasing as for lower values of the angular momentum.

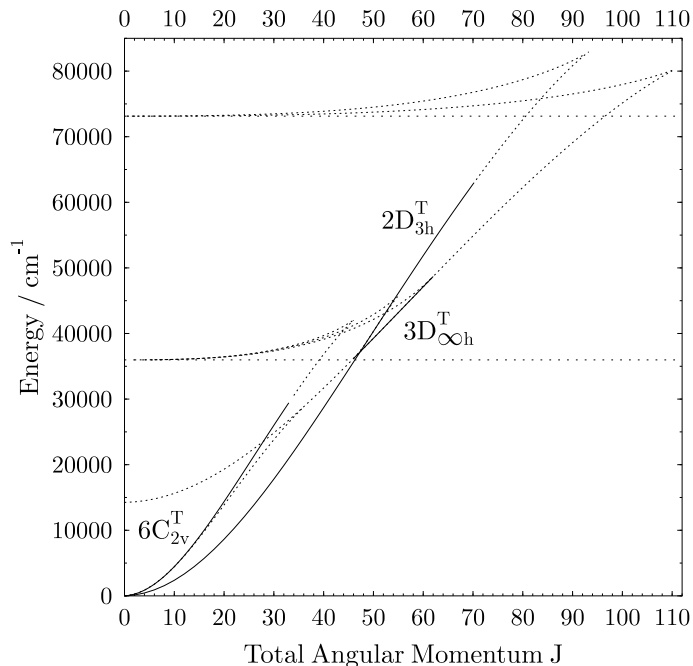


FIG. 1. The energies of linearly stable (solid lines) and unstable (dotted lines) relative equilibria of the H_3^+ ion are shown as functions of the total angular momentum J . The symmetry groups of the stable relative equilibria are indicated together with the degeneracy. The T-superscript in the symmetry group notation denotes that these groups include time reversal symmetries. They are isomorphic to the corresponding point groups. The two horizontal dotted lines indicate the dissociation energies of the ion.

The fate of linearly stable relative equilibria with negative Hessian eigenvalues is usually a Hamiltonian Hopf bifurcation, i.e. as J increases the frequencies of two normal modes become equal and then complex, the normal modes simultaneously becoming unstable [17]. This happens not only to the rotating equilateral triangle relative equilibria of H_3^+ , but also to the relative equilibria corresponding to the maximum rotational energy of the J -multiplets, and to their analogues for H_2D^+ and D_2H^+ .

Ultimately all relative equilibria collide with matching rotational barriers to dissociation at sufficiently high J . However before this happens there is a considerable region of phase space containing bound classical trajectories, even above the dissociation limit. We hope that these will correspond to

interesting patterns in the quantum spectrum.

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