

metal $d\pi$ orbitals would decrease $\text{Ru}(d\pi) \rightarrow \text{CO}(\pi^*)$ π -back-bonding. Also, the added electron density in the normally empty ring $e_g(\pi^*)$ orbitals, in either $(d\pi, e_g(\pi^*))$ or $(d_{xy}, e_g(\pi^*))$ excited states, might weaken the bond to CO. A metal \rightarrow axial-ligand $(d, \text{CO}(\pi^*))$ CT also might be dissociative, but it is expected to lie at too high an energy, based on the position of $\text{CO}(\pi^*)$ in molecular orbital calculations.⁵ The (d, d_{z^2}) ligand field excited state, which is dissociative for at least purely σ -bonded ligands (see ref 15), is probably at too high an energy to be thermally accessible from $^3(\pi, \pi^*)$; calculations place the empty d_{z^2} orbital substantially above $d\pi$ and d_{xy} .⁵ However, (d, d_{z^2}) could lie in energy between the $^1(\pi, \pi^*)$ (Q) and Soret (B) states, with the $(d\pi, e_g(\pi^*))$ between $^1(\pi, \pi^*)$ and $^3(\pi, \pi^*)$. If so, the quantum yield for photodissociation with Soret-band excitation might be greater than with excitation in the Q bands, as was observed previously⁸ for $\text{RuTPP}(\text{CO})(\text{pip})$. However, as noted in Results, we did not

observe such an effect for $\text{RuTPP}(\text{CO})(\text{py})$. More studies on the possible wavelength dependence of the photodissociation yield would help to clarify this issue. Nonetheless, the proposal that a metal-to-ring (d, π^*) CT state is thermally accessible from $^3(\pi, \pi^*)$ in the $\text{RuP}(\text{CO})(\text{L})$ complexes readily explains our time-resolved measurements and the photodissociation behavior of the compounds.

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Origin of Intramolecular Torques in ICN Photofragmentation

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Hamilton's equations are used to determine the importance of nearest-neighbor repulsive forces compared with bending forces in recent classical trajectory calculations of ICN or C1CN photofragment rotation.

Photodissociation of a triatomic molecule is sufficiently complicated that it is a challenge to determine which of the several sources of fragment rotation are most important for a particular molecule. Several recent classical trajectory (CT) calculations consider this question. Two sources of photofragment rotation have been discussed in these papers, and comparisons have been made between experimental results and the results of the calculations, to learn which influences are of greatest importance in determining the rotational state of the fragment. A dissociation fragment rotates either because some of its rotation as part of the parent molecule is preserved through the dissociation event, or because a torque acts on the fragment during the dissociation and the fragment is accelerated by this torque. We are concerned in this note with processes within the dissociating molecule which accelerate the rotation of the fragment, which are the bending forces that arise from the same sources that provide them in a stable molecule, and the short-range repulsive forces which act to repel the diatomic fragment and the atom, which are unique to a dissociating molecule. A bibliography of recent work in this area of photochemistry can be found in a recent paper from one of the most active groups.¹

Origin of Fragment Rotation

It is generally accepted that the amount of rotation excited in CN from photodissociation of ICN (or C1CN) is determined by the conformation of the molecule in its ground state and in the excited state(s) reached in the absorption, and by the internal motions in the molecule in these states. Hess and Leone² have given a clear discussion of the several states involved in the photoabsorption by ICN.

To understand how the rotation of the fragment is generated during the dissociation it is natural to ask about the torques exerted on the fragment during the event; torques lead to increased angular velocities, and thus to increased angular momenta. In the general case, fragment rotation will be influenced by the motions of the

parent molecule prior to dissociation. This note is not a thorough examination of all sources of rotation, but we mention in passing that, for ICN in particular, the rotation of the parent molecule is not an important source of fragment rotation.³

The two suggested sources of torque arising in the dissociation were described as upper state bending forces and nearest-neighbor repulsive forces. In any real molecule, both sources may be present in the dissociation; how important they are in any mathematical model of dissociation may be assessed by determining, at any point on the trajectory, how much torque can be assigned to each of the sources. The functional forms of the interaction potentials used in the various calculations differ and so do the expressions for the torque. We first apply Hamilton's equations to a Hamiltonian in which there is no upper-state bending force and show that nearest-neighbor repulsion leads to a torque on the CN. Then we examine the Hamiltonians used in recent studies of this problem, and show that, although these Hamiltonians contain an exponential repulsion term, with none of the Hamiltonians do we find a clearly identifiable torque arising from the repulsive forces. The authors whose work we study here probably did not intend that such a bias should be present in their analyses.

To complete this section we quote two brief excerpts from recent papers which have given especially concise descriptions of the physical bases of exciting rotation in photodissociation. From ref 4 we take the following description of the bending force mechanism: "...the high 'temperature' in the fragment rotational distribution must be caused by the hill in the bending degree of freedom in the vicinity of the linear configuration". From ref 3 we take an apt description of the nearest-neighbor repulsion mechanism: "Final state interactions have also been proposed to be the cause of fragment rotational energy. For a triatomic dissociation $\text{ABC} \rightarrow \text{A} + \text{BC}$, the simplest view would hold that the repulsion between A and B will cause rotation in the BC fragment as long as the line joining A and B does not also contain

(1) Goldfield, E. M.; Houston, P. L.; Ezra, G. S. *J. Chem. Phys.* **1986**, *84*, 3120.

(2) Hess, W. P.; Leone, S. R. *J. Chem. Phys.* **1987**, *86*, 3773.

(3) Marinelli, W. J.; Sivakumar, N.; Houston, P. L. *J. Phys. Chem.* **1984**, *88*, 6685.

(4) Waite, B. A.; Helvajian, H.; Dunlap, B. I.; Baronavski, A. P. *Chem. Phys. Lett.* **1984**, *111*, 544.

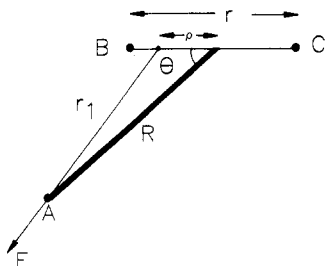


Figure 1. Coordinates used in the text. R is measured from the center of mass of BC. In the general case of repulsive forces acting between pairs (A,B) and (A,C), the reaction to the force shown acting on A will act on BC at a point a distance ρ from the center of mass. This force gives a torque if $\rho \neq 0$. In the case of "pure" NNR considered in the section Hamiltonian Functions (subsection a), the repulsion acts between A and B only, and there is no force on C. In this study, the distance r is fixed.

the BC center of mass". The Hamiltonians used in these two papers are among the ones we study shortly.

Hamilton's Equations and the Hamiltonians

For the three-atom system we are studying it is possible to choose a coordinate system that is more convenient than the Cartesian laboratory frame of reference; however, the Hamiltonian function $H(p,q)$ is elementary in the latter system. q_k and p_k are the positions and momenta of the atoms in the molecule. The equations of motion are Hamilton's equations:⁵

$$\dot{q}_k = \partial H / \partial p_k \quad \dot{p}_k = -\partial H / \partial q_k \quad (k = 1, \dots, 9)$$

By making several so-called canonical (or contact) transformations, the independent variables p_k and q_k may be transformed to the more convenient coordinate system shown in Figure 1 in which the equations of motion preserve their simple forms for the new coordinates and (conjugate) momenta.^{6,7} The Hamiltonian function becomes

$$H(P_R, j, l; R, r, \theta) = P_R^2 / 2\mu + l^2 / 2\mu R^2 + B(j)^2 + U(R, r, \theta)$$

in which the coordinate r , for the distance B-C, is fixed in our atom-rigid rotor approximation. B is the rotational constant for the B-C fragment, in our case, CN. The angular momentum that is of special interest for us is j , the angular momentum of the rigid rotor; the transformed Hamilton's equation for the pair of variables (j, θ) is

$$(j) = -\partial H / \partial \theta$$

which I call the "torque equation" because the rate of change of angular momentum of a body is equal to the torque. It is because of the separation of the fragment angular acceleration from other accelerations that we use these coordinates; the canonical form of Hamilton's equations is not preserved in arbitrary coordinate transformations, and the information we can obtain easily will not be readily available. This equation allows us to determine which part of the potential causes the torque and is therefore responsible for spinning the CN fragment. This will be illustrated next. Forces derived from the potential also accelerate the center of mass of the fragment and give another torque that leads to orbital angular momentum (l in the Hamiltonian) of I-CN; these are described by the other Hamilton's equations which are shown in ref 7.

Hamiltonian Functions

(a) *Nearest-Neighbor Repulsion (NNR)*. To illustrate the form of the expression for torque in NNR, we use a heuristic potential

from Pattengill.⁸ There is a repulsion between atoms A and B (as in Figure 1, but the force acts along the line between A and B).

$$U = A \exp(-kr_1)$$

Since the only θ -dependent terms in the Hamiltonian are in the potential energy, in this and subsequent examples we consider only the potential energy. To quote Pattengill, in this state, "the CN is in free rotation".⁸ $1/k$ is the range of the repulsion between A and B. There is no bending force in this potential, in the conventional sense, but if one writes this function in terms of the coordinates R and θ in Figure 1, the potential energy is anisotropic in θ :

$$U(R, \theta) = A \exp[-k(R^2 + \rho^2 - 2R\rho \cos \theta)^{1/2}]$$

The force acting on BC leads to a torque obtained from the torque equation:

$$(j) = \tau = kR\rho \sin \theta U / r_1$$

This form of the torque will obtain whether we have pure NNR as we consider here, or have a more general repulsion between A and BC as shown in Figure 1. The size of the torque depends on several variables:

- (i) On the range parameter. If $1/k$ is large—which implies a small force—then the torque is small.
- (ii) On the angle of the molecule. If $\theta = 0$, then there is no torque; at any other value of θ , there will be a torque. (We normally restrict the discussion to $\theta < 90^\circ$.)
- (iii) On the distance between the center of mass and the point where the force is applied. If $\rho = 0$ there is no torque.

It is an elementary exercise to show that the force

$$F = -\nabla U$$

exerted on A by BC is accompanied by a reaction force acting on BC which provides the same torque as we calculated more simply from the torque equation.

We examined this potential first to illustrate the essential features of a repulsion-driven torque. Next we consider other potentials that have been recently used in CT studies to determine to what extent the torques they produce have an origin in their repulsive potential term, among the several possibilities. Notice that when the potentials $U(R, r, \theta)$ are not separable into a sum of terms identifiable as arising from bending and repulsion, the torque we find using the torque equation is also not simply separable into a superposition of torques from those sources.

(b) *Reference 3*: $U(R, \theta) = A[1 + \theta_0^2 + k_2(\theta - \theta_0)^2] \exp(-k_1 R)$. Here, $1/k_1$ is the range of the repulsion and k_2 is the force constant for a harmonic bending potential centered on an equilibrium position θ_0 . (Coordinates from Figure 1.) The torque equation gives

$$\tau = 2k_2 A (\theta - \theta_0) \exp(-k_1 R)$$

from which we see that the torque is zero at $\theta = \theta_0$. Physically, one would expect a repulsion acting between A and B to give a torque for any nonlinear configuration. A zero torque might occur even if there were NNR, through cancellation of the repulsion-driven torque by a torque arising from bending forces. This cannot be the origin of the zero in the torque we are considering, however, since the location of the zero torque point ($\theta = \theta_0$) is unchanged even if the repulsive force disappears ($1/k_1 \rightarrow 0$).

Additionally, there is a torque in any other nonlinear configuration even if the range of the repulsion becomes infinite (so long as the bending force constant is not zero). The torque in this potential arises from the bending potential, not from the presence of the exponential repulsion. This potential, like that in part (a) is a heuristic potential, not based on any quantum-chemical calculation.

(c) *Reference 4*: $U(R, \theta) = A \exp(-kR) f(\theta)$.

$$f(\theta) = \exp(-4\theta^2) \quad (i)$$

(5) Goldstein, H. *Classical Mechanics*; Addison-Wesley: Reading, MA, 1959.

(6) Whittaker, E. A. *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies*, 4th Ed.; Cambridge University Press: New York, 1961; Chapter 13.

(7) Waite, B. A.; Dunlap, B. I. *J. Chem. Phys.* **1986**, *84*, 1391.

(8) Pattengill, M. D. *Chem. Phys.* **1983**, *78*, 229.

$$f(\theta) = \cos^2 9\theta, \quad \theta < 25^\circ$$

$$= 0.5, \quad \theta > 25^\circ \quad (\text{ii})$$

For the second of these two we find that the torque is as follows:

$$\tau = -18.4 \cos 9\theta \sin 9\theta \exp(-kR), \quad \theta < 25^\circ$$

$$= 0, \quad \theta > 25^\circ$$

In this potential the torque has zeros at $\theta = 0^\circ$, 10° , and 20° , and it is nonzero everywhere else in the range $0 < \theta < 25^\circ$ even if the exponential repulsion vanishes ($\exp(-kR) \rightarrow 1$). It is obvious that the torque does not arise from the repulsion. The potential in eq i is similar to the one considered next. Both of the potentials in this section are heuristic. Not surprisingly, the paper concluded that rotation arises from the action of the bending forces in their model and so in the molecule they studied, ClCN.

(d) Reference 7: $U(R, \theta) = A \exp(-kR) \exp(-\beta(R)\theta^2)$. $\beta(R)$ is a distance-dependent bending force constant. Using the torque equation one finds that the torque is (i) zero for the linear configuration, and (ii) greater than zero if the molecule is bent, even if the exponential repulsion vanishes.

The repulsion term, a function of the distance from atom A to the center of mass of BC, is not responsible for the torque. This potential is the result of fitting the above function to a quantum mechanical calculation of the potential function for ClCN. The absence of a torque due to the repulsive nearest-neighbor interaction is a consequence of the form of the function fitted to the potential. Using a different form of the potential would lead to a different dependence of torque on the constants k and β .

(e) Reference 1 presents a model calculation with considerable elaboration: hopping between surfaces is considered in the excited states and so there are several potential functions employed. (This shows how complicated the analysis of even this "simple" dissociation can be.) The potential energy term used in ref 1 is made up of the two adiabatic potentials coupled by an interaction term. We will not explore the full complexity of the model but we can examine the two potentials:

$$V_1 = A_1 \exp(-k_1 R) - C_6/R^6 + B_1 \theta^2 \exp(-\beta_1 R)$$

$$V_2 = A_2 \{\exp(-k_2 R - \gamma_2 \theta^2) + \theta^2 \exp(-\beta_2 R)\}$$

The first potential is associated with the state to which the molecule is excited by the absorption event, and the second is the potential of the bent excited state which correlates to $I(^2P_{3/2})$. The terms $B_1 \exp(-\beta_1 R)$ and $A_2 \exp(-\beta_2 R)$ are described as distance-dependent bending force constants. Potential V_1 gives no torque associated with the exponential repulsion even when $\theta \neq 0$; the torque depends on the bending force constant only. From V_2 we obtain a torque determined by two terms, one of which does not depend on the range of the exponential repulsion, $1/k_2$, and so cannot be a repulsion-driven torque. The other term defines a torque that decreases exponentially in the radial coordinate R with the range $1/k_2$ but which depends directly on the bending force constant γ_2 , vanishing when that constant is zero. Apparently, atom-diatom repulsion does not lead to rotation on this

surface although it will accelerate the center of mass of CN. The potentials used in this study were chosen on the grounds of physical plausibility rather than from a full potential calculation, and the authors treat several other aspects of the dissociation.

Summary

We have considered four potential energy functions that have been used in recent CT calculations of photofragmentation of ICN and ClCN; in each, there is an exponential repulsion energy term. In none of the four cases does the torque depend directly on the range parameter of the repulsion term in the way we have found for our "pure repulsion" case (Hamiltonian Functions, subsection a). This means that those calculations cannot correctly reflect the importance of NNR (or the more general form shown in Figure 1). In some cases, the torque is entirely independent of this range parameter, i.e., of the strength of the repulsive force. From the standpoint of valence-bond theories, a repulsive force localized between A and B, approximately, is entirely plausible. This seems to be tacitly accepted in most descriptions of the dissociation and is explicitly recognized in some, as a quotation given earlier shows.

The method employed here does not require the full trajectory calculation obtained by solving Hamilton's equations. We are able to make a general statement about torque at any point on the trajectory without solving the equations fully by focusing attention on the equation that gives—in the particular coordinates we employ—the angular acceleration of the diatomic fragment, and so from Newton's laws, the torque. The full trajectory calculations will be required to determine the rotational distribution following dissociation on any potential surface, and one should reach the same conclusions as ours by repeatedly calculating rotational distributions for various values of the parameters we have discussed. The present method is a shorter way to reach the limited conclusions we described.

In a recent elementary model calculation we have shown that features of the long-wavelength dissociation of ICN can be explained by nearest-neighbor repulsion effects exclusively.⁹ The angles involved in the bent upper-state configuration, which lead to torques from this source as illustrated in the section Hamiltonian Functions, subsection a, are moderate; for this reason it is hard to imagine that a correct analysis of rotational excitation in photodissociation can be obtained without consciously including this source among the possible sources of rotation. The calculations in which the repulsive forces do not give torques are still useful as limiting-case studies of dissociation in the presence of large bending forces. The problems described in this article will not be present in CT studies that use an interaction based on pairwise interactions of the three atoms.

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(9) Dugan, H.; Anthony, D. *J. Phys. Chem.* **1987**, *91*, 3929.