

Since $e_Q^{(2)}$ approaches $e_T^{(2)}$ as Q moves along p toward T and since E_Q approaches zero as s_Q approaches zero along any path it follows that the hypercircle C can be assigned a sufficiently small but nonzero radius that

$$|e_Q^{(2)} - e_T^{(2)}| < \frac{1}{2}|e_T^{(2)}| \quad (\text{A6})$$

for all Q on p that lie inside C, and such that

$$|\epsilon_Q| < \frac{1}{2}|e_T^{(2)}| \quad (\text{A7})$$

for any point within C whether it lies on p or not.

Now let X be a point on the line joining A to B. We wish to show that

$$E_X - E_T < 0 \quad (\text{A8})$$

for all X. Since $e_X^{(2)} \leq e_A^{(2)}$ it follows that

$$E_X - E_T \leq (e_A^{(2)} + \epsilon_X)s_X^2 \leq \{e_T^{(2)} + |e_T^{(2)} - e_A^{(2)}| + |\epsilon_X|\}s_X^2 \quad (\text{A9})$$

The desired result (A8) follows from (A9) after the introduction of the inequalities (A6) and (A7). This completes the argument.

References and Notes

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The Qualitative Behavior of Vibrational Excitation in Polyatomic Molecules

Yves Jean, Xavier Chapuisat, and Lionel Salem*

Contribution from the Laboratoire de Chimie Théorique, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France. Received October 21, 1974

Abstract. The vibrational excitation of polyatomic molecules by an atomic collider is studied in a simple static model (zero impact parameter, no rotational excitation). A general expression is derived for the external force F_i acting on the normal coordinate Q_i of the molecule. The behavior of F_i with angle(s) of approach is determined. Excitation of any of the three vibrational modes of a symmetric linear triatomic molecule XY_2 is shown to involve a nontrivial *blind angle*, for which $F_i = 0$ and vibrational excitation vanishes. The same is true for the A' mode (two blind angles) and one E' mode (one blind angle) of an equilateral symmetric triangular molecule X_3 approached in a plane perpendicular to the molecular plane. The theoretical and experimental implications on vibrational energy transfer are discussed.

The primary microscopic event in almost any reaction is that where the reactant acquires vibrational, rotational, and translational energy through collision with other molecules in the reactant vessel (whether they be other identical molecules, reactant partners, or solvent molecules). The greater part of the energy is acquired via vibrational excitation.

The collisional excitation of vibrations in a polyatomic molecule by an external atom is an extremely complex problem. The quantitative transition probabilities into the different sublevels of the various vibrational modes of the molecule depend on a vast number of factors:² (a) static factors such as the intermolecular potential function, and

the nature of the different normal modes of the molecule; (b) dynamic factors such as the collision energy, the impact parameter, and deflection angles. Inclusion, in accurate classical, semiclassical, or quantal calculations, of all these parameters, allows for estimates of vibrational excitation probabilities through numerical calculations.³ The complexity of the phenomenon, and therefore of the calculations required to describe it accurately, has clouded till now the insight into eventual laws which might govern its qualitative behavior. Our purpose has been to seek such laws, even at the cost of drastic but hopefully not unduly restrictive approximations. We feel that such laws should be particularly useful to organic chemists in their patient probing of the overall mechanism of chemical reactions.

In this paper we show how the relative vibrational excitation of the different modes of XY_2 (linear or bent) and X_3 triangular molecules depends on the angle of approach of the atomic collider.

1. A Static Approach to the External Forces Acting on the Vibrations of a Polyatomic Molecule

Our model is based on the following simplifying assumptions.

(1) The colliding atom is directed toward the center of gravity of the molecule (zero impact parameter and purely backward scattering). We therefore arbitrarily select, throughout this work, a specific family of collisions.

(2) No rotational excitation obtains in the collision. The angle of approach ϕ between the axis of approach and an axis related to the molecular framework is frozen once and for all at its initial value. This assumption should be reasonably valid for the interaction of a light collider with a heavy target molecule.

The first two assumptions reduce the ordinary *dynamical* treatment of the trajectory of the colliding atom, which would normally involve a time-dependent function $\phi(t)$, to a *static* treatment in which ϕ is a constant parameter.

(3) The intermolecular potential V is assumed to be a sum of central-force potentials between the impinging atom and each atom of the target molecule.

(4) Initially the target molecule is assumed to be in its vibrational ground state. Furthermore, throughout this work, the intramolecular distortions of the target molecule will be expressed in terms of unperturbed normal displacements.

Let us label the atoms of the target molecule A, B, C, D, etc. Let G be the position of the center of mass of the molecule. Finally M is the impinging atom. In a coordinate system with G as origin we label the Cartesian coordinates of A (x_A, y_A, z_A), those of B (x_B, y_B, z_B), etc., and those of M (x_M, y_M, z_M). The intermolecular potential V can be written

$$V = V_A(\rho_A) + V_B(\rho_B) + \dots \quad (1)$$

where ρ_A is the distance between A and M, ρ_B that between B and M, etc. The interatomic potential V_A is specific to the pair interaction between atoms A and M. Of course it depends on both M and A. Finally the normal modes of the target molecule are labelled Q_1, Q_2, Q_3 , etc.

The *force* acting on the nuclei in the i th normal mode is

$$F_i = -\partial V / \partial Q_i \quad (2)$$

Since each component of V depends only on one internuclear distance

$$\frac{\partial V}{\partial Q_i} = \frac{dV_A}{d\rho_A} \frac{\partial \rho_A}{\partial Q_i} + \frac{dV_B}{d\rho_B} \frac{\partial \rho_B}{\partial Q_i} + \dots \quad (3)$$

In terms of the Cartesian coordinates defining the position of atoms A and M

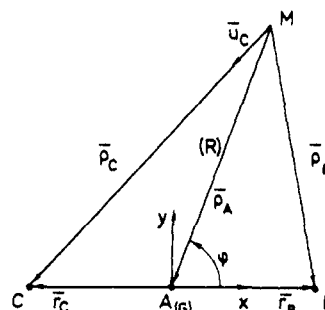


Figure 1. General coordinate system for attack of M on linear CAB. Coordinates in parentheses refer to the center of gravity.

$$\rho_A = [(x_A - x_M)^2 + (y_A - y_M)^2 + (z_M - z_M)^2]^{1/2} \quad (4)$$

Whence

$$\frac{\partial \rho_A}{\partial Q_i} = \frac{1}{\rho_A} \left[(x_A - x_M) \frac{\partial x_A}{\partial Q_i} + (y_A - y_M) \frac{\partial y_A}{\partial Q_i} + (z_A - z_M) \frac{\partial z_A}{\partial Q_i} \right] \quad (5)$$

Since x_A, y_A , and z_A are also the Cartesian components of the vector $\mathbf{r}_A = \mathbf{G}-\mathbf{A}$ linking the center of mass to atom A, and $(x_A - x_M), (y_A - y_M)$, and $(z_A - z_M)$ are the components of the vector $\mathbf{M}-\mathbf{A} = \rho_A$, we have finally

$$\frac{\partial V}{\partial Q_i} = V_A' \frac{\rho_A}{\rho_A} \frac{\partial \mathbf{r}_A}{\partial Q_i} + V_B' \frac{\rho_B}{\rho_B} \frac{\partial \mathbf{r}_B}{\partial Q_i} + \dots \quad (6)$$

where V_A' is the first derivative $dV_A/d\rho_A$ of the interatomic potential V_A . In compact notation we have the general expression for the force acting on the normal coordinate Q_i .

$$F_i = - \sum_{\text{all atoms } N} V_N' \mathbf{u}_N \cdot \frac{\partial \mathbf{r}_N}{\partial Q_i} \quad (7)$$

In (7) \mathbf{u}_N is a unit vector on the axis (ρ_N) linking the colliding atom M to an atom N of the target molecule. In the approximation below, both vectors in (7) are evaluated at the equilibrium configuration of the molecule.

Equation 7, which will be used henceforth, shows that the only information required for calculating the external forces is: (1) the form of the interatomic potentials V_N ; (2) the position of the collider M relative to the atoms A, B, C, ..., which determines the direction of the unit vectors \mathbf{u}_N ; (3) the vectors $\partial \mathbf{r}_N / \partial Q_i$ ($N = A, B, \dots$) whose components ($\partial x_N / \partial Q_i, \partial y_N / \partial Q_i, \partial z_N / \partial Q_i$) depend solely on the manner in which the *Cartesian coordinates* of the atoms vary with the *normal coordinates*. The form of such vectors is well known for all polyatomic molecules with simple symmetry, and can be identified with the arrows in the drawings of molecular normal modes by Herzberg.⁴

2. The Linear Symmetric Triatomic Molecule XY_2

Figure 1 shows the coordinate system for an atom colliding with a symmetric linear triatomic molecule CAB in which the masses of B and C are equal, and for which the center of mass G is identical with A at equilibrium. We call R the distance between M and the center of gravity G (here R happens to be equal to ρ_A) and l the equilibrium distance $G-B = G-C$. Since M is aimed at G, the distortions of interest are limited to the (x, y) plane. The position of M is uniquely defined by the pair of parameters R and ϕ .

The normal modes Q_1, Q_2 , and Q_3 , with the corresponding Cartesian displacements, are recalled in Figure 2.⁴ These Cartesian displacements define the components of $\partial \mathbf{r}_A / \partial Q_i, \partial \mathbf{r}_B / \partial Q_i$, and $\partial \mathbf{r}_C / \partial Q_i$ ($i = 1, 2, 3$) which are also shown in the figure. At the same time the components, at equilibrium, of the vectors $\mathbf{u}_A, \mathbf{u}_B$, and \mathbf{u}_C are respectively

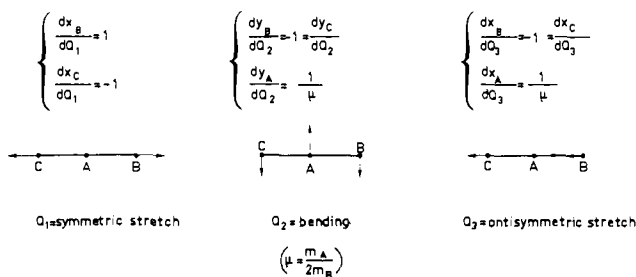


Figure 2. Normal coordinates of a symmetric linear triatomic molecule. The changes in Cartesian coordinates are given explicitly.

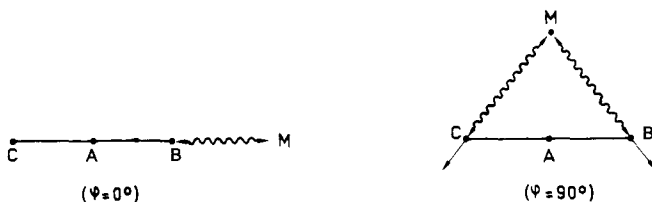


Figure 3. Forces induced by M in the triatomic molecule at 0 and 90° (curly arrows indicate strong interactions).

$$\mathbf{u}_A \begin{Bmatrix} \frac{-R \cos \phi}{\rho_A} \\ -R \sin \phi \\ \frac{-R \sin \phi}{\rho_A} \end{Bmatrix} \mathbf{u}_B \begin{Bmatrix} \frac{l - R \cos \phi}{\rho_B} \\ -R \sin \phi \\ \frac{-R \sin \phi}{\rho_B} \end{Bmatrix} \mathbf{u}_C \begin{Bmatrix} \frac{-l - R \cos \phi}{\rho_C} \\ -R \sin \phi \\ \frac{-R \sin \phi}{\rho_C} \end{Bmatrix} \quad (8)$$

It is then a simple matter to calculate the scalar products in eq 7 and the three forces

$$\begin{aligned} F_1(\phi) &= -l \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) + R \cos \phi \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \\ F_2(\phi) &= R \sin \phi \left[\frac{1}{\mu} \frac{V_A'}{\rho_A} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right] \\ F_3(\phi) &= l \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) + \\ &\quad R \cos \phi \left[\frac{1}{\mu} \frac{V_A'}{\rho_A} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right] \end{aligned} \quad (9)$$

In these formulas the dependence of the forces on ϕ occurs both *explicitly* and *implicitly* via ρ_A , ρ_B , and ρ_C which are themselves functions of ϕ and R ,

$$\begin{aligned} \rho_A &= R \\ \rho_B &= R(1 - 2\epsilon \cos \phi + \epsilon^2)^{1/2} \quad \epsilon = l/R \\ \rho_C &= R(1 + 2\epsilon \cos \phi + \epsilon^2)^{1/2} \end{aligned} \quad (10)$$

Equations 9 and 10 yield the exact forces acting on each normal mode, within our initial assumptions.

The qualitative behavior of these forces obtains immediately from eq 9. Let us make the reasonable assumption that at the distance of closest approach the potentials V_A , V_B , and V_C are all repulsive potentials, described by rapidly varying (for instance, exponential) functions of distance. Hence, for the limiting values $\phi = 0$ and 90° the dominant term in F_1 , F_2 , and F_3 is determined respectively by V_B' and by V_A' , i.e., the potential involving the atom closest to the collider. Thus

$$\begin{aligned} F_1(0^\circ) &\approx \frac{V_B'}{\rho_B} (R - l) < 0; \\ F_1(90^\circ) &\approx -l \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) > 0 \end{aligned} \quad (11)$$

It is clear from (11) that the force F_1 on the symmetric stretching mode must *vanish* for a certain angle ϕ_1 between

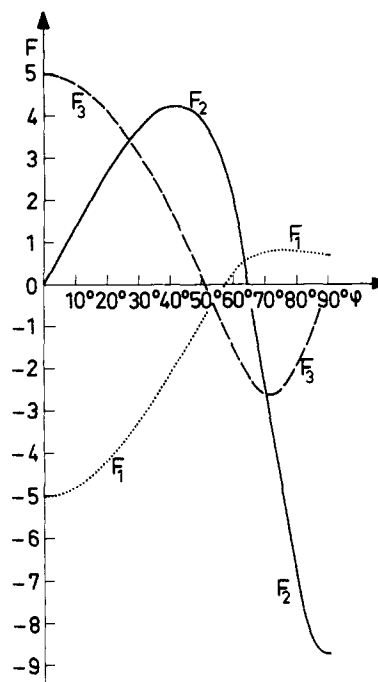


Figure 4. Variation of the forces on the normal coordinates Q_1 , Q_2 , and Q_3 , as a function of impact angle ϕ .⁶

0 and 90° . For this angle there will be no excitation of the ν_1 vibration whatever the strength of the collision. A simple explanation for this result is as follows (Figure 3). For $\phi = 0^\circ$, atom B is compressed toward A by the incoming collider and Q_1 is excited with negative amplitude (opposite to the arrows in Figure 2). For $\phi = 90^\circ$, atoms B and C are both repelled, with a force component pushing them away from each other; Q_1 is excited with positive amplitude. At some intermediate angle Q_1 is not excited at all.

In a similar manner F_2 , which of course vanishes for $\phi = 0^\circ$, behaves as

$$\begin{aligned} F_2(\phi \rightarrow 0^\circ) &\approx -\phi R \frac{V_B'}{\rho_B} > 0; \\ F_2(90^\circ) &\approx \frac{R}{\mu} \frac{V_A'}{\rho_A} < 0 \end{aligned} \quad (12)$$

Hence the force F_2 acting on the bending mode vanishes, not only trivially for a collinear attack, but *also* for a certain angle ϕ_2 between 0 and 90° . The reader will easily find a rationalization of this result similar to the previous one; ν_2 (as drawn in Figure 2) is excited with positive amplitude for small values of ϕ but with negative amplitude at 90° .

Finally F_3 , which vanishes for $\phi = 90^\circ$, behaves as⁵

$$\begin{aligned} F_3(0^\circ) &\approx -\frac{V_B'}{\rho_B} (R - l) > 0; \\ F_3(\phi \rightarrow 90^\circ) &\approx \frac{R}{\mu} \left(\frac{\pi}{2} - \phi \right) \frac{V_A'}{\rho_A} < 0 \end{aligned} \quad (13)$$

The force F_3 acting on the antisymmetric stretching mode vanishes both at 90° and *also* at a certain angle ϕ_3 between 0 and 90° .

Our main result is that for each vibrational mode there exists at least one "blind" angle for which the vibrational excitation vanishes. Figure 4 shows the accurate variation of the forces with impact angle ϕ . These curves correspond to an assumed common potential

$$V_A \equiv V_B \equiv V_C \equiv Ke^{-\alpha\rho} \quad \alpha = 5 \text{ \AA}^{-1}$$

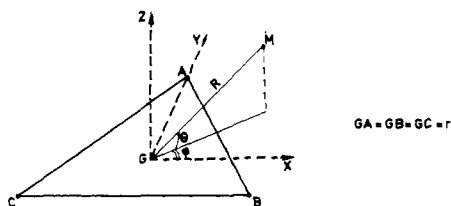


Figure 5. General coordinate system for attack of M on triangular ABC.

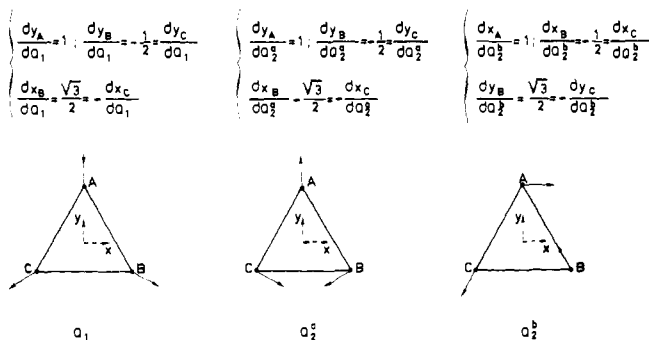


Figure 6. Normal coordinates of an equilateral symmetric triangular molecule. The changes in Cartesian coordinates are given explicitly.

a collision energy E_C such that $K/E = 10^4$ (see Appendix II), $l = 1.2 \text{ \AA}$, and $\mu = 0.375$ (viz., CO_2). The blind angles are then

$$\begin{aligned} \text{for } Q_1 \text{ and } F_1 & \quad \phi_1 = 57.5^\circ \\ \text{for } Q_2 \text{ and } F_2 & \quad \phi_2 = 64^\circ \text{ (and } 0^\circ) \\ \text{for } Q_3 \text{ and } F_3 & \quad \phi_3 = 52^\circ \text{ (and } 90^\circ) \end{aligned} \quad (14)$$

In (14) the "trivial" blind angle values are given in parentheses.

3. The Equilateral Symmetric Triatomic Molecule X_3

We now turn to the approach of an atom M to the center of gravity of an equilateral symmetric triangular molecule ABC. The approach is characterized by the distance R between M and the center of gravity G, and by two polar angles θ and ϕ which specify the orientation of the vector G-M (Figure 5). Also $G-A = G-B = G-C = r$.

The three normal modes are shown in Figure 6.⁴ One, Q_1 , is the totally symmetric A_1' mode, while Q_2^a and Q_2^b are a pair of degenerate components of an E' stretching mode. The figure also shows the Cartesian displacements in these modes. The components at equilibrium of the unit vectors pointing from M to A, B, or C are respectively

$$\mathbf{u}_A \begin{pmatrix} \frac{-R \cos \theta \cos \phi}{\rho_A} \\ \frac{r - R \cos \theta \sin \phi}{\rho_A} \\ \frac{-R \sin \theta}{\rho_A} \end{pmatrix} \quad \mathbf{u}_B \begin{pmatrix} \frac{r\sqrt{3}/2 - R \cos \theta \cos \phi}{\rho_B} \\ \frac{-r/2 - R \cos \theta \sin \phi}{\rho_B} \\ \frac{-R \sin \theta}{\rho_B} \end{pmatrix} \quad \mathbf{u}_C \begin{pmatrix} \frac{-r\sqrt{3}/2 - R \cos \theta \cos \phi}{\rho_C} \\ \frac{-r/2 - R \cos \theta \sin \phi}{\rho_C} \\ \frac{-R \sin \theta}{\rho_C} \end{pmatrix} \quad (15)$$

The scalar products $\mathbf{u}_{N'} \cdot (\partial r_N / \partial Q_i)$ of eq 7 follow immediately and yield the forces as follows

$$\begin{aligned} F_1 &= -r \left(\frac{V_A'}{\rho_A} + \frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) + \\ & \quad R \cos \theta \left[\frac{1}{2} \sin \phi \left\{ 2 \frac{V_A'}{\rho_A} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right\} + \right. \\ & \quad \left. \frac{\sqrt{3}}{2} \cos \phi \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \right] \\ F_2^a &= -r \left\{ \frac{V_A'}{\rho_A} - \frac{1}{2} \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right\} + \\ & \quad R \cos \theta \left[\frac{1}{2} \sin \phi \left\{ 2 \frac{V_A'}{\rho_A} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right\} - \right. \\ & \quad \left. \frac{\sqrt{3}}{2} \cos \phi \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \right] \\ F_2^b &= r \frac{\sqrt{3}}{2} \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) + \\ & \quad R \cos \theta \left[\frac{\sqrt{3}}{2} \sin \phi \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) + \right. \\ & \quad \left. \frac{1}{2} \cos \phi \left\{ 2 \frac{V_A'}{\rho_A} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \right\} \right] \quad (16) \end{aligned}$$

Again the dependence on θ and ϕ occurs both explicitly and implicitly via the distances ρ_A , ρ_B , and ρ_C .

Equation 16 for the forces induced on the three normal modes of a symmetric triangular molecule ($A \equiv B \equiv C$) allows us to obtain immediately the behavior for certain limiting cases,

(a) For an approach to G perpendicular to the molecular plane

$$\begin{aligned} (\theta = \pi/2, \quad \phi = \pm\pi/2) \\ F_1 \approx -r \left(\frac{V_A'}{\rho_A} + \frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \\ F_2^a \equiv 0, \quad F_2^b \equiv 0 \end{aligned} \quad (17)$$

Only Q_1 is excited. The two degenerate modes are unaffected. Indeed such an attack can only "expand" the molecule as a whole. Since $V_A' = V_B' = V_C'$ at this particular approach, unsymmetrical distortions cannot be excited.

(b) For an in-plane approach toward an atom A, with whom the interaction potential dominates relative to the two others

$$\begin{aligned} (\theta = 0, \quad \phi = \pi/2) \\ F_1 \approx \frac{V_A'}{\rho_A} (R - r); \quad F_2^a \approx \frac{V_A'}{\rho_A} (R - r); \quad F_2^b = 0 \end{aligned} \quad (18)$$

In this approximation, the symmetric mode and one component of the degenerate mode are excited *equally*. Inclusion of V_B' and V_C' would of course distinguish between F_1 and F_2^a .

(c) For an in-plane approach toward a bond BC, with which the two interaction potentials dominate relative to the third one

$$\begin{aligned} (\theta = 0, \quad \phi = -\pi/2) \\ F_1 = \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \left(\frac{1}{2} R - r \right); \\ F_2^a = \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \left(\frac{1}{2} R + \frac{1}{2} r \right); \quad F_2^b = 0 \end{aligned} \quad (19)$$

Again only Q_1 and Q_2^a are excited. However, the degenerate stretching mode is much more strongly excited than the symmetric stretching mode. Indeed the approaching atom repels B and C roughly in directions perpendicular to the

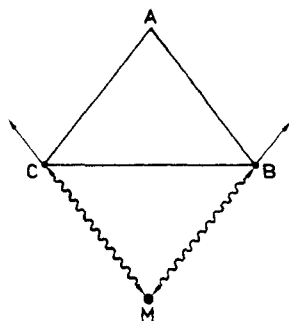


Figure 7. Forces induced by M in the triangular molecule for an in-plane attack toward a bond. (Curly arrows indicate strong interactions.)

bonds BA and CA. Under these conditions Q_1 is hardly excited, while Q_2^a is strongly impulsed with a large negative amplitude (Figure 7).

Of course selective excitation, in the last two processes, of F_2^a rather than F_2^b is just a simple consequence of our arbitrary choosing attack along the y axis. The situation is reversed for two other values of ϕ between $-\pi/2$ and $\pi/2$. For an in-plane attack at other ϕ angles both Q_2^a and Q_2^b will be excited.

Let us now turn to the qualitative behavior of the forces as the angles θ and ϕ vary, and first to the variation with azimuthal angle ϕ for an in-plane attack ($\theta = 0$). The results are shown in Figure 8. The force F_1 on the symmetric mode oscillates, with periodicity $2\pi/3$, between a maximum value (eq 18) and a minimum value (eq 19). At its maximum F_1 is negative. The sign of F_1 at its minimum depends on the sign of $((R/2) - r)$; except for relatively strong collisions this factor should be positive; whatever the case the force F_1 comes very close to vanishing at $-\pi/2$, $\pi/6$, etc. (Figure 8).

The forces F_2^a and F_2^b on the two degenerate modes oscillate with a periodicity 2π . However, the correct periodicity for the energy transfer to any mode, as determined by the symmetry of the molecule, must be $2\pi/3$. Indeed it is possible, for each angle ϕ , to construct combinations of Q_2^a and Q_2^b

$$\begin{aligned} Q' &= -\cos 2\phi Q_2^a + \sin 2\phi Q_2^b \\ Q'' &= -\sin 2\phi Q_2^a - \cos 2\phi Q_2^b \end{aligned} \quad (20)$$

such that Q' and Q'' have the proper symmetry of the problem. Therefore in Figure 8 we also plot the forces

$$\begin{aligned} F' &= -\cos 2\phi F_2^a + \sin 2\phi F_2^b \\ F'' &= -\sin 2\phi F_2^a - \cos 2\phi F_2^b \end{aligned} \quad (21)$$

These forces have the proper periodicity $2\pi/3$.

The other interesting behavior is the manner in which excitation varies with polar angle θ for an atom M arriving toward an apex ($\phi = \pi/2$) or toward a bond ($\phi = -\pi/2$). We need only consider F_1 and F_2^a since by symmetry F_2^b vanishes. The limiting values of F_1 and F_2^a are respectively those given by eq 17 for $\theta = \pi/2$ and by eq 18 and 19 for $\theta = 0$. The force on the symmetric mode is positive at 90° but negative at 0° , whether for attack on an atom or for attack on a bond (in the latter case, we assume $(R/2) - r > 0$). Hence F_1 has a blind angle for approach to an apex atom, and also a blind angle for approach to the center of a bond. We can expect the dead angle θ_1^A for the apex attack to be larger (around 60°) than that $\theta_1^{BC} = 30\text{--}40^\circ$ for the attack on a bond, since in the latter case the limiting value F_1 ($\theta = 0^\circ$) is very close to zero. The value of θ_1^{BC} should also be

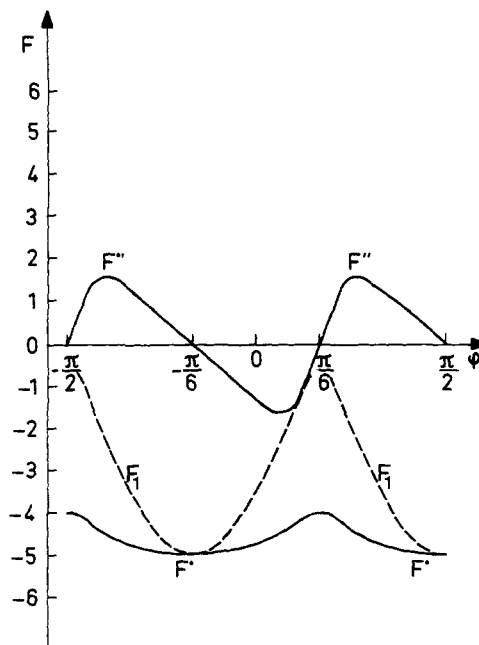


Figure 8. Variation of the forces acting on the normal coordinates Q_1 , Q' , and Q'' , as a function of azimuthal angle ϕ for an in-plane attack.

subject to large fluctuations due to the uncertainty on $(R/2) - r$.

Finally the force F_2^a on the E' mode vanishes for perpendicular attack and is negative for in-plane attack, both for $\phi = \pi/2$ and for $\phi = -\pi/2$. Since the value $\theta = \pi/2$ does not correspond to any special symmetrical situation for Q_2^a (see Figure 6; the xz is not a plane of symmetry) this zero value for F_2^a must be the boundary of a positive region. Hence there should be an additional, nontrivial, blind angle, not far from the vertical approach, for excitation of Q_2^a , corresponding to the second boundary of the positive region. Whether this blind angle occurs on the side of atomic attack ($\phi = \pi/2$) or the side of bond attack ($\phi = -\pi/2$) will depend on the values of the numerical parameters.

These results are confirmed in Figure 9, which shows the variation of F_1 and F_2^a with θ . For the numerical parameters of section 2 and $r = 0.9$, the blind angle for F_2 occurs for apex attack

$$\theta_2^A = 64^\circ \quad (\text{and } \theta_2 = \pi/2)$$

while the two blind angles for F_1 are respectively

$$\begin{aligned} \theta_1^A &= 62^\circ \\ \theta_1^{BC} &= 34^\circ \end{aligned}$$

4. Consequences for Energy Transfer and Comparison with Experiment

We now attempt to investigate the possible physically observable consequences of the force curves and blind angles. A full numerical calculation of translation-to-vibration (T-V) energy transfer probabilities would be unrealistic in the framework of the assumptions of section 1. Since our emphasis has been on the orientational dependence of the force field, the most immediate consequence of our results will appear in the so-called "steric factor".⁷ This steric factor arises in the expression for the T-V energy transfer

$$\Delta E(\theta, \phi) \propto \left| \int_{-\infty}^{\infty} f[R(t), \theta, \phi] \exp(i\omega t) dt \right|^2 \quad (22)$$

in which $f(t)$ is a normalized force whose maximum value is unity. The averaging of ΔE over all angles requires an inte-

gration over angles which, when done separately, yields a number called the steric factor. For the collision of an atom with a molecule this factor is given by

$$sf = \frac{1}{4\pi} \int \int F(\theta, \phi)^2 \sin \theta \, d\theta \, d\phi \quad (23)$$

where $F(\theta, \phi)$ is the normalized value of the force. The traditional approach to the calculation of sf has been to assume a monotonic trigonometric angular dependence of the force F on the angles θ and ϕ . For the collision of an atom with a linear triatomic, this leads to steric factors

$$sf(\nu_1) = \frac{1}{3}, \quad sf(\nu_2) = \frac{2}{3}, \quad sf(\nu_3) = \frac{1}{3}$$

where ν_2 is the single in-plane excitable bending mode.

We have applied eq 23 using the correct forces calculated in this paper (eq 9). The steric factors can be obtained by integration of the force curves of Figure 4. The calculated values are

$$sf(\nu_1) = 0.091, \quad sf(\nu_2) = 0.186, \quad sf(\nu_3) = 0.133$$

Two important conclusions emerge from these numbers. (a) The steric factors are all approximately three times *smaller* than previously assumed. This is of course due to the blind angles and corresponding zero values in the force curves. (b) The ratio of the steric factor for ν_2 and ν_1 remains very close to 2, but the steric factor for ν_3 is now roughly *three-halves* that for ν_1 .

The predicted difference in the steric factors for ν_1 and ν_3 should result in an observable difference in excitation probabilities, or conversely relaxation times, for *very fast* collisions ($e^{\omega t} \approx 1$) at high energies (no coupling of T-V transfer with translation-to-rotation (T-R) transfer). The experimental situation for the relaxation of linear triatomics, with particular emphasis on CO_2 , in the presence of rare gases, is still undecided. Measurements with different experimental techniques are widely at variance.^{2,8} However, Taylor and Bitterman⁸ conclude that "although the question is not completely closed, the sum total of all the experimental evidence indicates that from 300 to 6000°K the vibration relaxation of modes ν_1 plus ν_2 and ν_3 of CO_2 are the same to within a factor of 2".

At present, therefore, direct comparison of our theory with experiments on CO_2 is hampered by these experimental uncertainties. Furthermore it should be noticed that the observed phenomena for CO_2 include two effects which we have not accounted for in our model: (a) the very fast vibrational energy exchange between ν_1 and ν_2 ;⁹ (b) the *intramolecular* vibrational relaxation and excitation. As more experimental results become available for other triatomic molecules, in which the first effect need not be present, it will be possible to test our prediction of higher excitability of ν_3 than ν_1 .

5. Discussion

We will not return to the crucial assumptions which were developed in the first section. Several other implicit assumptions, which may have escaped the reader, should be mentioned.

The primordial role ascribed to the center of gravity G of the target molecule, rather than to that of the ensemble target plus M , is coherent with the assumption of frozen impact angles. Both assumptions imply that M is light relative to the mass of the target molecule.

The calculated forces are purely functions of three-dimensional coordinates (R, θ, ϕ) ; they have been derived without any symmetry restriction. However, if one were to use the fundamental eq 7, 9, or 16 to calculate actual vibrational *energy transfers*, the constraint of fixed orientation

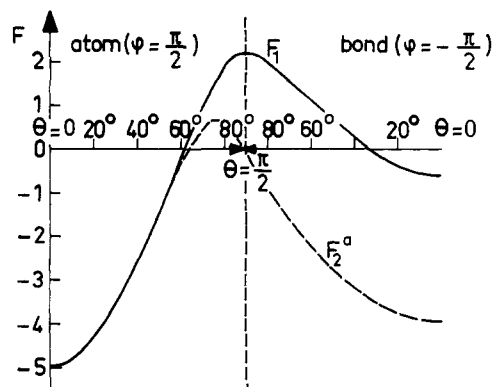


Figure 9. Variation of the forces acting on the normal coordinates Q_1 and Q_2^a as a function of polar angle θ for an out-of-plane attack. Left-hand side indicates attack toward atom A, right-hand side indicates attack toward bond BC.

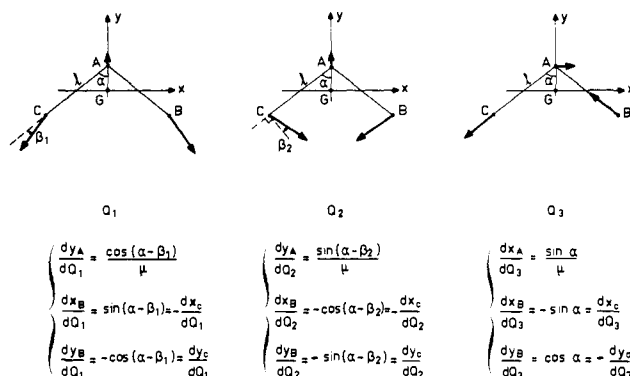


Figure 10. Normal coordinates of a symmetric nonlinear triatomic molecule. The changes in cartesian coordinates are given explicitly.

(θ, ϕ) for the relative motion would constitute a severe restriction requiring further discussion.

Rigorously the force acting on a given normal mode depends not only on (R, θ, ϕ) but on the actual amplitude of the various Q_i 's. Here these amplitudes have been assumed to be sufficiently small, as caused by collisions at thermal energies, so as to have only higher order effects on the calculated forces.

In spite of the stringent limits which are imposed on our model, we feel that some insight has been gained as to the detailed, orientational behavior of vibrational excitation from the ground state for a few very simple systems. We have shown that excitation of *any of the three* vibrational modes of a symmetric linear triatomic molecule involves a nontrivial blind angle. For collision with an equilateral symmetric triangular molecule there are two blind angles for excitation of the A' mode, and one nontrivial blind angle for excitation of the E' mode. As we have seen, the observable consequences of these blind angles should eventually be verifiable by experimental investigation.

Acknowledgment. The authors are grateful to Dr. Guy Bergeron for some pertinent suggestions.

Appendix I

Both particular types of molecules above (linear AB_2 ($D_{\infty h}$) and triangular A_3 (D_{3h})) can be considered as limiting cases of the more general nonlinear AB_2 molecule (C_{2v}). By making use of the same coordinates R, θ , and ϕ as in Figure 5 and the notations defined in Figure 10 for the normal modes, the final expressions for the forces are the following.

$$\begin{aligned}
F_1 = & -l \left\{ \frac{V_A'}{\rho_A} \frac{\cos \alpha \cos (\alpha - \beta_1)}{\mu(1 + \mu)} + \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \times \right. \\
& \left. \left(\sin \alpha \sin (\alpha - \beta_1) + \frac{\mu}{1 + \mu} \cos \alpha \cos (\alpha - \beta_1) \right) \right\} + \\
& R \cos \theta \left\{ \left(\frac{1}{\mu} \frac{V_A'}{\rho_A} - \frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \sin \phi \cos (\alpha - \beta_1) + \right. \\
& \left. \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \cos \phi \sin (\alpha - \beta_1) \right\} \\
F_2 = & -l \left\{ \frac{V_A'}{\rho_A} \frac{\cos \alpha \sin (\alpha - \beta_2)}{\mu(1 + \mu)} - \left(\frac{V_B'}{\rho_B} + \frac{V_C'}{\rho_C} \right) \times \right. \\
& \left. \left(\sin \alpha \cos (\alpha - \beta_2) - \frac{\mu}{1 + \mu} \cos \alpha \sin (\alpha - \beta_2) \right) \right\} + \\
& R \cos \theta \left\{ \left(\frac{1}{\mu} \frac{V_A'}{\rho_A} - \frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \sin \phi \sin (\alpha - \beta_2) - \right. \\
& \left. \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \cos \phi \cos (\alpha - \beta_2) \right\} \\
F_3 = & l \left\{ \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \left(\sin^2 \alpha + \frac{\mu}{1 + \mu} \cos^2 \alpha \right) \right\} + \\
& R \cos \theta \left\{ \left(\frac{1}{\mu} \frac{V_A'}{\rho_A} - \frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \cos \phi \sin \alpha + \right. \\
& \left. \left(\frac{V_B'}{\rho_B} - \frac{V_C'}{\rho_C} \right) \sin \phi \cos \alpha \right\}
\end{aligned} \tag{24}$$

The angles β_1 and β_2 in Figure 10 and eq 22, whose values depend on the nature of the atoms A and B and the valence force constants, are obtainable from standard expressions in normal mode theory (cf. ref 4, eq II, p 193). It is readily verified that eq 22 simplify to eq 9 and 16 through respectively

$$\alpha = 90^\circ, \quad \beta_1 = \beta_2 = 0, \quad \theta = 0 \text{ (in-plane attack)}$$

and

$$\alpha = 30^\circ, \quad \beta_1 = -30^\circ, \quad \beta_2 = 0, \quad \mu = \frac{l}{2}, \quad l = r\sqrt{3}$$

Appendix II

The numerical curves showing the variation of the forces with angle of approach are obtained as follows. In all the numerical applications of the present article, the potential describing the interaction between the atoms in the mole-

cule and the impinging atom M is taken as a unique exponential function

$$V_N(\rho_N) = K \exp(-\alpha\rho_N), \quad (N = A, B, \dots)$$

where

$$\alpha = 5 \text{ \AA}^{-1}$$

Let us consider the case of the linear AB_2 molecule (cf. eq 9). The approximate model discussed in the first section allows us to write

$$E_{\text{coll}} = [V_A + V_B + V_C]_R \tag{25}$$

where E_{coll} is the collision energy and R is the distance of closest approach. For a given angle of approach ϕ , it is possible to obtain R numerically as a solution of eq 25, for an arbitrarily chosen value of E_{coll} . Only the ratio K/E_{coll} is physically significant; $K/E_{\text{coll}} = 10^4$ is used throughout the article and corresponds to a weak collision energy. Thus it becomes possible to calculate the forces F_i ($i = 1, 2, 3$), at the distance of closest approach, as functions of ϕ , since $R(\phi)$ was obtained previously and the other quantities in (9) are either molecular constants (l, μ) or simple functions of R such as $\rho_A, \rho_B, \rho_C, V_A', V_B',$ and V_C' .

References and Notes

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- (5) For $\phi \rightarrow 90^\circ$, the first term of F_3 ($B \equiv C$) yields $2V_B'l^2((\pi/2) - \phi)/R^2$ which is also proportional to $((\pi/2) - \phi)$, but with a smaller ($V_B' \ll V_A'$) proportionality constant.
- (6) Of course, the excitation energies, contrary to the forces, keep a constant sign. However, they also vanish at the angles where the forces vanish.
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