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Note on the Interatomic Spacings in the Ions I_3^-, FHF$^-$*

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The ions I_3^-, FHF$^-$ may be considered to be formed from a neutral molecule, I_2 or HF respectively, bound to a negative ion, I^- or F^- respectively. We consider the energy of the molecule when the distance between the two extreme atoms is held fixed, but the central atom is allowed to move along the line joining the extreme atoms. We use the analogy of the molecule H_3, for which calculations have been made. When the distance between extreme atoms is below a certain critical distance, there is a single minimum for the energy of the molecule, as a function of the position of the central atom, midway between the two other atoms. When the distance between extreme atoms is greater, there are two minima, one nearer one extreme atom, the other nearer the other, as if a diatomic molecule and an ion were being formed. The experimental evidence indicates that in most compounds containing the ion I_3^-, the unsymmetrical case corresponds to the observed structure, though one compound, tetraphenyl arsonium triiodide, is known, in which we find the symmetrical case.

The ions I_3^- and FHF$^-$ resemble each other in that each one can be considered to arise from an ion, I^- and F^- respcetively, and a neutral molecule, I_2 and HF respectively. Compounds containing these ions have been the subject of a good deal of experimental work. The ions are approximately linear, the hydrogen being between the fluorines in FHF$^-$. In I_3^-, there is a slight deviation from linearity, which could arise from steric effects from other atoms in the crystal, and the distances from the central iodine to the other two are different, except in one compound, tetraphenyl arsonium triiodide. The FHF$^-$ ion appears to be linear and with equal spacings.

Pimentel (1951) has given a brief theoretical discussion of a molecular orbital interpretation of these ions, in the case in which we assume an equispaced linear configuration. The more interesting feature, however, is the unequal spacing found in the triiodides, and it is not hard to see why such a situation could be expected. Let us denote the atoms by *a*, *b*, *c*, in order, and let us consider the energy of the ion if *a* and *c* are held fixed at a given distance *D* from each other, and *b* is allowed to move between *a* and *c* on the line joining them. If *D* is very large, *b* will have two separate equilibrium positions, whose distances from *a* will be called d_1, d_2 (where $d_1 \leq d_2$). The atom *b* in this limit will form a diatomic molecule (I_2 or HF respectively) with the atom near it, leaving the other atom as a negative ion. As *D* decreases, these two separate energy minima will coalesce, forming a single minimum when *D* becomes less than a certain critical value. This general behavior is made clearer by a very simple case in which calculations have been made: the linear case of the molecule H_3. This is not strictly analogous; H_3^-, which has not been calculated, would be closer. Nevertheless we expect in H_3 too that for a fixed *D*, the energy will show a single minimum as a function of the position of the hydrogen atom *b* if *D* is small enough, and a double minimum if it is larger.

The calculations for H_3 have been made by Hirschfelder, Diamond & Eyring (1937). In Fig. 1 we give a contour plot of the energy of the molecule as a function of d_{ab} and d_{bc}, the distances between atoms

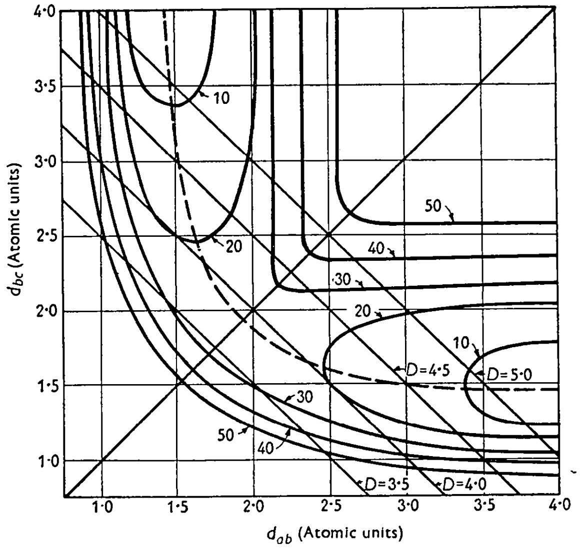

Fig. 1. Energy contours for linear configuration of H_3, according to Hirschfelder, Diamond & Eyring (1937). Distances d_{ab} and d_{bc} (in Bohr atomic units) are those between extreme atoms, *a* and *c*, and central atom *b*. Energies given in k.cal. The straight line with 45° slope corresponds to $d_{ab} = d_{bc}$, and those with negative 45° slope correspond to D $(= d_{ab}+d_{bc})$ equal to 3·5, 4, 4·5, 5 units respectively. Dashed line corresponds to locus of minimum energies.

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a and *b*, and *b* and *c* respectively, taken from Fig. 1 of the paper of Hirschfelder, Diamond & Eyring (1937). The zero of energy is taken to be the state of a hydrogen atom at infinite distance from a hydrogen molecule. The dashed line in Fig. 1 indicates the locus of the minima of the two valleys corresponding to an unsymmetrical configuration consisting of a molecule and an atom. This locus passes over a saddle point or pass where the dashed line intersects the 45° line $d_{ab} = d_{bc}$; the energy at this point is about 25 kcal. This represents the energy of activation, the minimum energy which the molecule must have in order that the central atom may pass from being bound to one extreme atom to being bound to the other. It was to investigate this energy of activation that the calculation of Hirschfelder, Diamond & Eyring (1937) was made.

We can, however, look at the calculations in a way more adapted to the present problem. In Fig. 1 we show four lines, with 45° negative slope, corresponding to $d_{ab}+d_{bc} = D = 3{\cdot}5$, 4, 4·5, and 5 atomic units respectively. We can read off the graph the values of energy for each of these values of *D*, as a function of d_{ab}. In this way we get the information which we have plotted in Fig. 2, where we show the energy as a function of d_{ab}, for these four values of *D*. The formation of the double minimum as *D* increases is very obvious.

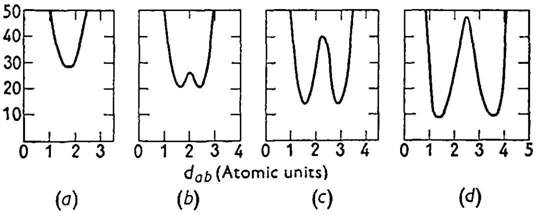

Fig. 2. Energy of the linear H_3 emolcule, as function of d_{ab}, position of inner hydrogen atom, for the four values of *D*, the distance between the extreme atoms, given in Fig. 1. Data scaled from Fig. 1.

At the same time, we note that the distance d_1 from the extreme hydrogen to the nearer energy minimum of the central hydrogen is considerably greater than the distance $1{\cdot}40a_0$ found in the hydrogen molecule, except for the largest values of *D*. This is shown directly in Fig. 3. Here we show the positions of the two minimum distances, d_1 and d_2, as functions of *D*, the distance between extreme hydrogens. Below the critical distance there is only one minimum position, at *D*/2.

In an accompanying paper, Dr R. C. L. Mooney Slater (1959) has reported on new measurements for tetraphenyl arsonium triiodide, and has collected the values of d_1 and d_2 as functions of *D* for all cases in which the triiodide group has been measured by X-ray methods. In her Figs. 5(*a*) and 5(*b*) she plots the data as we have done in Fig. 3 for hydrogen. The resemblance of the graphs is striking. The data indicate that in tetraphenyl arsonium triiodide, we have almost exactly the value of *D* at which the two minima d_1 and d_2 coalesce, whereas in other observed cases *D* is slightly larger, and d_1 and d_2 are distinct. On the other hand, since d_1 and d_2 seem to be equal in the FHF$^-$ ion, we may assume that the value of *D* found in this ion equals the critical value, or is slightly less, whereas in I_3^- we sometimes have distances slightly greater than the critical value.

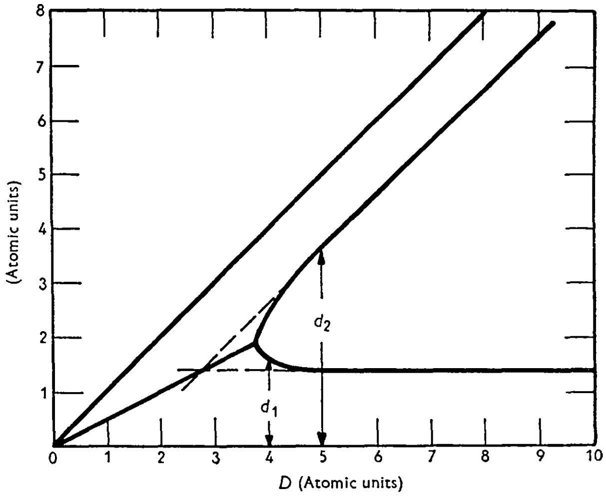

Fig. 3. Distances d_1 and d_2 from one extreme hydrogen to energy minima of inner hydrogen, as function of distance *D* between extreme hydrogens. Data scaled from Fig. 1.

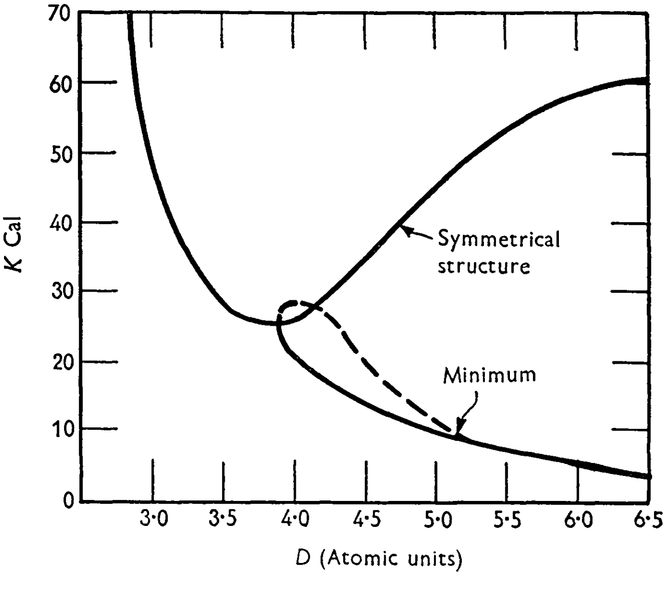

Fig. 4. Energy of linear H_3 molecule, from data of Fig. 1, as function of *D*, distance between extreme atoms. Curve marked 'symmetrical structure' is for case where inner hydrogen is centrally located. Curve marked 'minimum' is for case where inner hydrogen is at one of the two unsymmetrical minima shown in Fig. 2. Dashed curve represents hypothetical case in which there is a real minimum of energy, rather than a saddle point, corresponding to lowest energy of symmetrical structure.

We may next inquire what determines the value of D, and hence determines whether we are in the range where there are two minima, or a single one. If the central atom b is at its equilibrium distance d_1 or d_2 for a given D, the energy of the whole ion I_3^- or FHF^-, or of the H_3 molecule which we have been using as a simplified analogue, will be a function of the distance D between the extreme atoms a and c. In Fig. 4 we show this energy as a function of D, for H_3, again read off from the contours of Fig. 1. There are several curves shown in Fig. 4. First, we give the energy as a function of D for the case where $d_1 = d_2 = D/2$, or the symmetrical structure. This curve shows a minimum, corresponding to the saddle point or pass, and then rises again to a plateau at large values of D, corresponding to the energy of three separated hydrogen atoms at infinite distances from each other. The second curve, which joins this one at its minimum, represents the energy at the bottom of the minimum shown in Fig. 2. It is the energy at the point where the straight line $D =$ constant intersects the dashed line in Fig. 1. It represents the lowest possible energy for the molecule, with the given distance D between the extreme atoms. We see that as D increases, the energy continually decreases, so that H_3 does not form a stable structure, but rather a hydrogen atom will be repelled as it approaches a hydrogen molecule. This disregards the very slight attraction which will be produced at large values of D on account of the Van der Waals attraction, which will presumably stabilize a complex H_3 into the form of a molecule H_2 and a rather widely separated H atom, with an energy very slightly less than that at infinite values of D.

The behavior shown by the full lines of Fig. 4, and the calculations of Hirschfelder, Diamond & Eyring (1937), is not the only one which would be possible for the case of H_3. As those authors remark, a simpler approximation for the same problem indicates that there might be a true minimum, not a saddle point, of the energy at the minimum value consistent with the symmetrical structure. In this case, the energy which would be found passing along the dashed line of Fig. 1 would first rise, as d_1 and d_2 separated from each other, and then would fall again as we went over two separate passes down into the valleys corresponding to diatomic molecules. The activation energy would correspond to the energy at the top of these two passes. Such a situation is sketched schematically in the dashed line of Fig. 4.

The situation which would be found in I_3^- and FHF^- may be expected to be different, on account of the negative charge on the ion. An ion I^- approaching a molecule I_2 will polarize the molecule, and this in turn will produce a dipole field at the I^- ion, which will attract it, considerably more strongly than the Van der Waals attraction would do. Hence we may conclude that the ion I_3^-, as a function of D, with the central atom at its equilibrium at each value of D, will have a stable form at a certain value of D. We might have curves behaving schematically like those of Fig. 5, where we have again drawn two cases corresponding to the two shown in Fig. 4. It should be understood that these curves of Fig. 5 are not the result of calculation, but merely surmises based on our experience with the case of H_3.

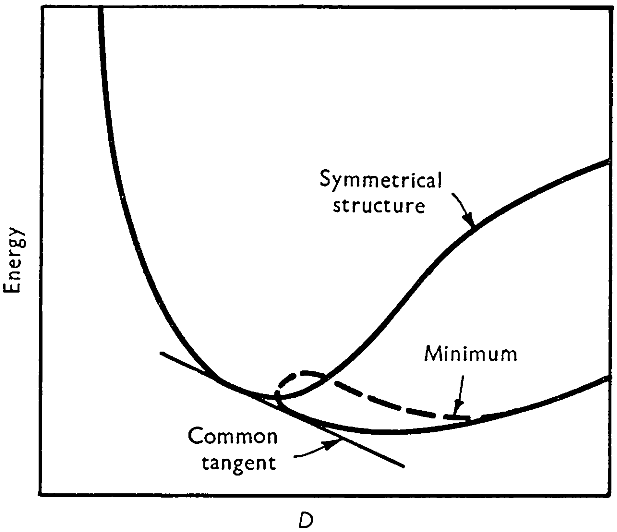

Fig. 5. Hypothetical curves similar to Fig. 4, for ions such as I_3^- in which there is attraction between ion and atom at large values of D.

We observe that for each of the hypothetical curves of Fig. 5, there is a minimum of energy for a value of D greater than the critical value. For the case shown by the dotted line, there is another minimum exactly corresponding to the critical value. In this case, there is no *a priori* way of deciding which of the two minima should have lower energy. It seems plausible that the curves for I_3^- and FHF^- might resemble some modification of those shown in Fig. 5. If we had the form shown by the continuous curve of Fig. 5, corresponding to the case found in H_3, the stable form of the ion would correspond to an unsymmetrical structure, with a value of D greater than the critical value. If the ion were under some pressure from its surroundings, the value of D would be decreased; a given external pressure corresponds to a negative slope of the curve of energy versus D, and the greater the pressure, the greater the negative slope, and hence the less D is. If the slope is such as to form a common tangent to the two branches of the curve, as shown in Fig. 5, two forms would simultaneously be stable, one corresponding to D slightly greater than the critical value, one slightly less. For greater pressures than this, only the symmetrical form would be stable. The situation would be rather similar for the other case, shown by the dashed line in Fig. 5.

In the case of the triiodide, it may be that the minimum energy comes at approximately the largest

D observed in crystals, and that the case of tetraphenyl arsonium triiodide, in which the D is the smallest observed experimentally, and in which the two minima have coalesced, is the one in which the ion is subjected to greatest pressure from its environment. The fact that d_1 and d_2 are observed to be equal in the FHF^- ion would suggest that here we might have the case shown by the dotted line in Fig. 5, but with the minimum of energy corresponding to the symmetrical structure lying lower than the unsymmetrical one. The reason for the difference between the two cases could not be understood without a detailed numerical calculation.

The arguments given here do not depend on the details of the method used to calculate the wave functions of the triatomic ion. Such a calculation, as a matter of fact, would be extremely complicated, and no adequate calculations have yet been made, except for H_3. A simple molecular orbital treatment would be far from adequate; L. C. Allen (unpublished) has shown that even to get an adequate wave function for HF requires extensive configuration interaction. But there is no doubt that a calculation, if properly made, combining molecular orbital and covalent methods by means of configuration interaction, would show the general behavior given in Figs. 1, 2, and 3.

It is worth pointing out that the situation as illustrated for H_3 in Figs. 1, 2, and 3, and discussed with respect to I_3^- and FHF^- in the present note, does not fit in with the simplest conception of resonance, which implies that an atomic arrangement leading to resonating electronic structures should be stabler than one without resonance. In the present case, if the central atom is midway between the extreme ones, or if $d_{ab} = d_{bc} = D/2$, two resonating structures are possible, with covalent bonds between atoms a and b, or between b and c. The lowering of energy on account of this resonance, or configuration interaction, is then greatest with this symmetrical arrangement. However, when D is greater than the critical distance, the total energy is lower if the central atom takes up an antisymmetrical position nearer one or the other of the extreme atoms. The reason is that the single bond which can be formed under these circumstances is so much stronger than if the atom were in the central position that the total energy is lowest for the unsymmetrical position. This situation was pointed out by Hirschfelder, Diamond & Eyring (1937) with reference to the case of H_3. It shows that the idea of resonance does not necessarily lead to a symmetrical arrangement in such cases as we are considering.

We may note that the arguments presented in the present paper are similar to what would be used to discuss a hydrogen bond, in which usually we have the situation shown in Fig. 2(c) or (d), with the hydrogen definitely closer to one of the neighboring atoms. Of course, if the two neighboring atoms are unlike, or in dissimilar environments, or if there are cooperative effects as in the ferro-electric crystals such as potassium dihydrogen phosphate, one of the minima will become lower than the other, and in such a case the hydrogen will lie in the lower of the two minima. Considerations of this general nature have been given by Lippincott & Schroeder (1955), who give a curve resembling our Fig. 3 for the O–H distance as a function of the O–O distance. In Fig. 6, we give a graph showing this case of the hydrogen bond, plotted in the same way in which Fig. 3 was constructed. The experimental points given on this graph are taken from the review paper of Shull & Wollan (1956), and include several observations which were not available to Lippincott & Schroeder (1955). The similarity of this case to the others we have been considering is obvious. As in this case of the hydrogen bond, we should expect that in the triiodide crystals, the environment will have the effect of stabilizing one of the minima more than the other, so that in the actual crystals the central iodine atom is definitely bound to one of the other iodines, not to the other.

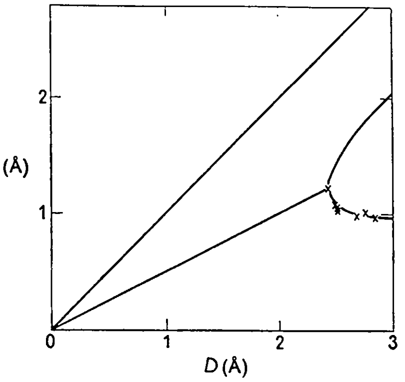

Fig. 6. Experimental values of distances from hydrogen to the two oxygens, as function of distance D between extreme oxygens, in the hydrogen bond. Data from Table 2, Shull & Wollan (1956).

I am indebted to Prof. R. C. Lord for having called my attention to the interesting case of FHF^-, and to Dr R. C. L. Mooney Slater for valuable discussions regarding I_3^-.

References

Hirschfelder, J., Diamond, H. & Eyring, H. (1937). *J. Chem. Phys.* **5**, 695.

Lippincott, E. R. & Schroeder, R. (1955). *J. Chem. Phys.* **23**, 1131.

Mooney Slater, R. C. L. (1959). *Acta Cryst.* **12**, 187.

Pimentel, G. C. (1951). *J. Chem. Phys.* **19**, 446.

Shull, C. G. & Wollan, E. O. (1956). *Solid State Physics*, vol. II, p. 137. New York: Academic Press.