On an Anomaly in the Mobility of Gaseous Ions

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Many mobility versus field curves for gaseous ions show a high mobility "bump" just above the ohmic range. The effect arises from the nature of the force between ions and molecules. It is effectively attractive for low speeds of encounter and repulsive for high speeds. A partial cancellation of deflections occurs in a range of intermediate speeds; the scattering cross section then appears to be abnormally low.

I. INTRODUCTION

The first semiquantitative understanding of the motion of gaseous ions in electric fields was achieved by Langevin.[1] He adopted as a model force between the ions and the gas molecules a superposition of the attractive polarization force and a hard core repulsion. He then applied kinetic theory to the mixture of ions and molecules and determined the response of the ions in such a mixture to a small field. A drift velocity proportional to the field was the result. The constant of proportionality is called the mobility. Langevin produced the first estimates for this number.

There has been no essential departure from Langevin's approach in subsequent years, but only refinements and extensions; they occurred generally in close correlation with experiment.[2-5] A useful extension was the one to high fields. One gets then a drift velocity versus field curve rather than a simple constant of proportionality. In favorable cases, the analysis of such data has been carried out in a quite satisfactory way.[†] The general rule is that if the results are expressed in terms of a mobility, then the mobility tends to decrease with increasing

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† See Refs. 6 and 7. In Ref. 6, the abscissas on Figs. 3–7 are a power of ten too small.

field. The qualitative explanation of this trend is that high fields raise the mean random velocity of the ions above their thermal value. The mean speed of encounter of ions and molecules is thereby also increased. Under those conditions the mean free time between collisions would remain a constant only for inverse fifth power forces (Maxwellian molecules), but decrease for stiffer forces. This is normally the case in practice, except in the limit of very slow encounters when the polarization force prevails.

It is the purpose of this paper to focus attention on the "mobility bump" which is observed occasionally in a mobility versus field plot. While the mobility generally behaves as described in the preceding paragraph, there is sometimes found a short range of fields for which the mobility rises before the drop sets in.[4,8–10] The explanation proposed for this effect is the following. The drift velocity of the ions is controlled by their encounters with the molecules; these depend in turn on the mutual force. This force is attractive at long range and repulsive at short range. If one studies the momentum transfer cross section for such a force as function of speed one finds that it has a "dip" at intermediate speeds as compared to the limiting laws for high or low speed. The reason for this dip is a partial compensation of attraction and repulsion. The latter is responsible for the high speed behavior, and the former for low speed behavior. However, attraction and repulsion bend the path in the opposite sense, or give phase shifts of opposite sign. Hence a compensation with anomalous transparency must be expected for a small range of speeds. If these speeds are just slightly larger than thermal under the experimental conditions employed, a "bump" type anomaly will appear in the data. Furthermore the bump will be larger if the repulsive force is soft. The reason for this is that a soft repulsion can compensate the polarization attraction over a wider range of speeds than a hard force.

II. A STUDY OF CROSS SECTIONS

Computations of drift velocities and comparisons with experiment are presented in Section III. In this section, we show the effect of the compensation phenomenon on the behavior of the momentum transfer cross section, employing two simple models.

Within the range of validity of classical mechanics the momentum transfer cross section $\sigma(v)$ is defined as

$$\sigma(v) = 2\pi \int_0^\infty (1 - \cos \chi) b \, db. \tag{1}$$

Here b is the impact parameter for a collision, and χ is the angle of deflection in the center of mass frame. For the discussion of this section, we may think of the mobility as being inversely proportional to the quantity (1).

The first model to be discussed is the so-called Langevin force, consisting of the polarization force as the attractive force and a hard sphere radius as the repulsion. The deflection equals

$$\chi = 2 \int_0 \frac{b\,du}{\left\{1 - b^2u^2 + \dfrac{e^2P}{mv^2}u^4\right\}^{\frac{1}{2}}} - \pi. \tag{2}$$

Here P is the polarizability of the molecules and u an integration variable which equals the reciprocal radius. The upper limit of the integral is the smaller positive root of the denominator or $1/a$ whichever is less; a is the radius of the hard core. Formula (2) gives rise to a variety of elliptic integrals which one can teach a computer to distinguish and to look up in its library. After this is done, the integration (1) has to follow; this was carried out numerically. Results are shown in Fig. 1 in a log-log plot. On abscissa is V which equals

$$V = \left(\frac{m}{P}\right)^{\frac{1}{2}} \frac{a^2}{e} v. \tag{3}$$

It is a scaled dimensionless speed whose adjustable parameter is the hard sphere radius a. On ordinate is the cross section Σ in units πa^2. The curve is entirely determined by its two asymptotes. The equations for the asymptotes are

$$\Sigma = 2.210/V \tag{4a}$$

for the polarization force, and

$$\Sigma = 1 \tag{4b}$$

for the hard sphere repulsion.

Observation of Fig. 1 shows that a simple interpolation between the two straight lines, say, by adding the two cross sections, does not reproduce the actual behavior of the cross section even qualitatively. As the speed increases from very low values the cross section departs from the polarization value by being lower, not higher. The effect is admittedly small; the cross section falls to 85 percent of the polarization value and behaves normally as regards the hard sphere value: it approaches it from above.

To show up the effect more clearly, the calculation was repeated for

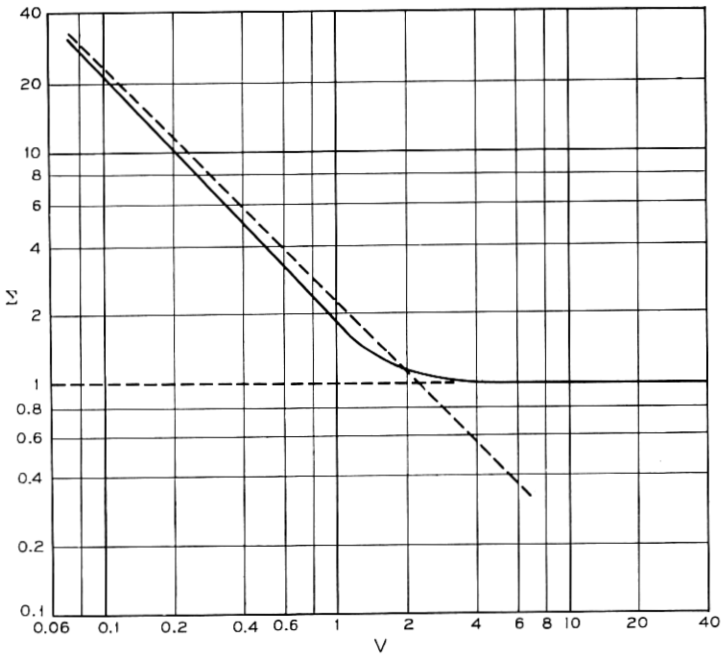

Fig. 1 — Momentum transfer cross section versus speed for the Langevin force. Cross section is relative to hard sphere, speed is rendered dimensionless through (4). Cross section falls below one limiting law (asymptote) albeit by a small amount.

another force model: the same polarization force plus a $1/r^6$ repulsive potential. The reason for this choice was that it is an extremely soft repulsion; so the two models should bracket the truth. An incidental advantage is that no orbit calculations are required because the angle of deflection is again an elliptic integral. In detail, the potential U was taken in the form

$$U = \tfrac{1}{2}e^2P\left\{-\frac{1}{r^4} + \frac{a^2}{r^6}\right\}. \tag{5}$$

a is the distance at which the potential vanishes, and thus resembles vaguely the hard core radius of the first example. With the help of standard mechanics, one finds for the angle of scattering

$$\chi = \int_{s_1}^{\infty} \frac{b\,ds}{\left(s^3 - b^2s^2 + \dfrac{e^2P}{mv^2}\,s - \dfrac{e^2P}{mv^2}\,a^2\right)^{\frac{1}{2}}} - \pi. \tag{6}$$

s is an integration variable which equals the square of the radius; the other letters have the same meaning as previously. s_1 is the largest positive root of the denominator. The integral thus is a complete elliptic integral. It takes two different forms, depending on whether the denominator has three real roots or one real root. One can teach a computer to find the roots from Cardano's formula and to look up the elliptic integral in its library. Once χ is found, the momentum transfer cross section (1) is computed in the same way as in the first example.

Results are shown in Fig. 2 on a log-log plot similar to Fig. 1. The parameter V defined in equation (3) is again used as abscissa, and the ordinate is again the cross section in units πa^2. On a log-log plot the curve has again two asymptotes representing high speed and low speed behavior. The equations for the asymptotes are

$$\Sigma = 2.210/V \tag{7a}$$

and

$$\Sigma = 1.112/V^{\frac{2}{3}}. \tag{7b}$$

They represent respectively the cross section which would prevail if the polarization force or the repulsive force were present alone.

This time the effect under discussion is very large. The curve for the cross section approaches either asymptote from below; in the central region it is substantially smaller than it would be according to either limiting law. The reduction is to 75 percent of the repulsive cross section and 36 percent of the polarization cross section.

Before comparing these results with experiment, we shall look at the theory internally and compare the two model cases with each other. The effect under discussion arises because there are strongly bent orbits which finally result in a small deflection; the reason is that bending toward and away from the center cancel. Langevin was aware of this effect.[1] In his Fig. 4, the fourth from the axis of the eleven orbits shown is of that nature. His results also contain the bump in the mobility curve. His Fig. 7 is essentially a plot of mobility versus speed. However, the effect is small. Our second example shows that if the repulsive force is made soft the effect can become very large. So it is rather the smallness of the effect for the Langevin force which needs some extra attention here. The effect is small because the model is discontinuous. Orbits which approach the hard core ever so closely do not experience any repulsion, and hence no cancellation leading to anomalously small angles. On the other hand, orbits colliding with the core do experience the attraction. But, once present, the repulsion predominates very quickly,

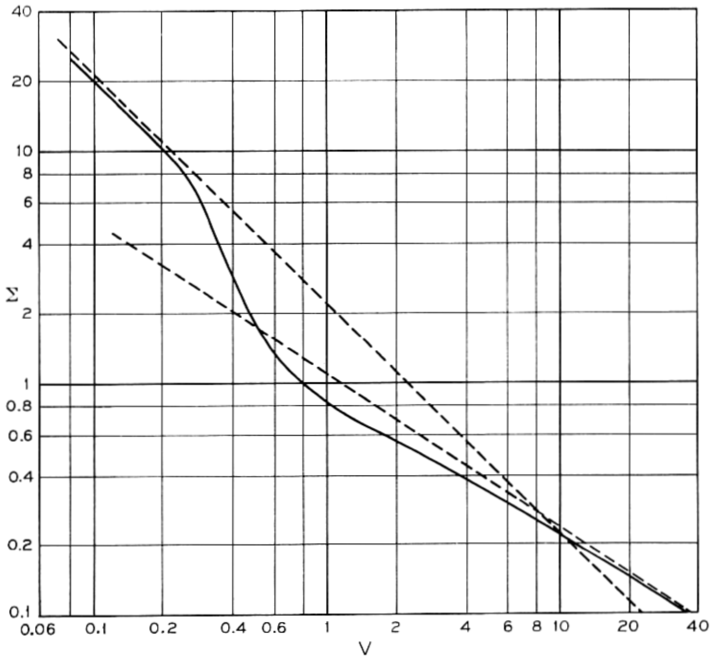

Fig. 2 — Momentum transfer cross section versus speed for the 4–6 potential. Abscissa and ordinate are essentially as in Fig. 1. Cross section falls very far below both limiting laws (asymptotes). Strong effect arises from softness of repulsion.

and the opportunity for small angle deflections is limited. In Fig. 3 a typical plot of deflection versus impact parameter is shown. The angle itself is a continuous function, but its derivative is infinite for orbits just barely touching the hard sphere. The effect under discussion arises from the small angles in the neighborhood of the point where the angle passes through zero. This is very close to the point having infinite derivative; hence, the relevant angular range is very small. If the repulsive force is softer, Fig. 3 will become smooth, and look somewhat like Fig. 4. Clearly, the range of initial conditions for which the angle of scattering is anomalously small will be much larger for such a situation.

III. COMPARISON OF THEORY AND EXPERIMENT

It is an essential feature of the "mobility bump" that it is observed outside the ohmic range. A simple mobility calculation is thus not quite right, but one should carry out an "intermediate field" type of

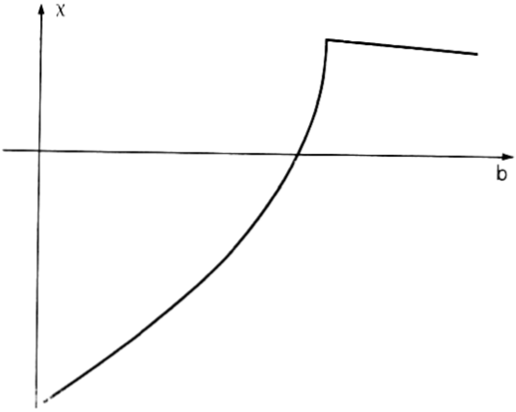

Fig. 3 — Detail on the dependence of the scattering angle on the impact parameter for the Langevin force. Infinite slope discontinuity inherent in the model makes also the passage through zero very rapid.

calculation.[6] However, as the bump appears at the very edge of the ohmic range, a mobility calculation should be indicative of precise results. What drives the drift velocity out of the ohmic range is the increase of the random speed of the ions above the thermal value. This speed can be very reliably estimated using experimental information only. As the first step, we "unreduce" a plot giving the reduced mobility as function of E/p_0, in order to determine the observed drift velocity v_d. This is accomplished with the help of the formula

$$v_d = 760 \frac{E}{p_0} \mu_0 . \tag{8}$$

Thereupon we determine the mean square velocity by a formula which

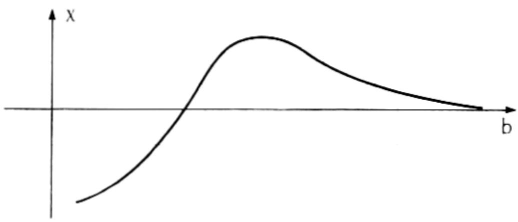

Fig. 4 — Detail on the dependence of the scattering angle on the impact parameter for the 4–6 potential. Curve is continuous and the passage through zero slower than in Fig. 3.

is discussed extensively elsewhere*

$$\langle v^2 \rangle = \frac{3kT}{m(\text{ion})} + \left(1 + \frac{m(\text{gas})}{m(\text{ion})}\right) v_d^2 . \tag{9}$$

What we need further on is the root mean square *relative* speed which we shall simply call "the speed" and denote by v:

$$v = \left\{ \frac{3kT}{m(\text{gas})} + \langle v^2 \rangle \right\}^{\frac{1}{2}} \tag{10}$$

which comes out to be

$$v = \left\{ \frac{3kT + m(\text{gas}) v_d^2}{m} \right\}^{\frac{1}{2}} . \tag{11}$$

Here m is the reduced ion-molecule mass as used previously.

We may use equation (11) to convert the experimental data into a plot giving reduced mobility versus speed. Such a plot is shown in semilog form in Fig. 5 for H_3^+ in H_2 as published in Ref. 9. The plot shows the conventionally reduced mobility as function of the logarithm of the speed v.

We are in a position to find theoretical data which can be compared with a curve such as Fig. 5. The results on cross sections obtained in Section II can be exploited to yield a mobility μ with the help of the formula

$$\mu = \frac{1}{3} \frac{e}{mN} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{v^2}{\sigma(v)} \right) \right\rangle^{\dagger} . \tag{12}$$

Here e is the charge of the ion, m the reduced mass of the ion-molecule system and N the number density of the gas. $\sigma(v)$ is the momentum transfer cross section as defined in equation (1). In addition, a calculation of Hershey can also be brought in for comparison.[5] Hershey carried out calculations of mobilities for a ninth power repulsive force in combination with the polarization force. His result as shown in curve II, Fig. 7, Ref. 5, is of the desired form. His abscissa, labelled $1/\mu$, is the random velocity (10) of this paper, apart from a scale factor. His ordinates

* See equation (21.20) of Ref. 7 or equation (122) of Ref. 6. Equation (97) of Ref. 6 also shows an instance in which the formula is not rigorously valid. Yet it still holds to within 5 percent.

† The formula is a modification of (20.10) of Ref. 7 for an isotropic situation. It also appears as (21.17), or results from (21.35). All three derivations fall short of being general. Indications are that the formula is close but not exact. Compare the comments to (168) of Ref. 6 where the same formula appears with a slightly different numerical factor.

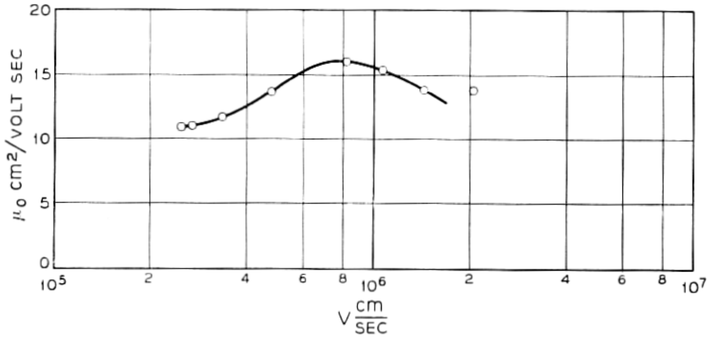

Fig. 5 — Adaptation to theoretical analysis of the data of Miller and others, on the motion of H_3^+ in H_2. Ordinate is the same as in the original paper, but on abscissa is plotted the root mean square speed of encounter.

must be multiplied with a factor to yield the polarization mobility at zero speed for the system under consideration.

In Figs. 6, 7 and 8 are shown the reduced mobilities predicted for H_3^+ in H_2 , using hard sphere repulsion, seventh power repulsion and ninth power repulsion, respectively, combined with the polarization attraction. On abscissa is the mean speed of encounter; the speed is plotted logarithmically, so that scale factors have no influence on the shape of the curves. Their only adjustability consists in a possible horizontal rigid displacement.

Comparison of the three theoretical curves among themselves bears out the point made at the end of the introduction. The bump is largest in Fig. 7 for which the repulsion is softest, and smallest in Fig. 6, for the

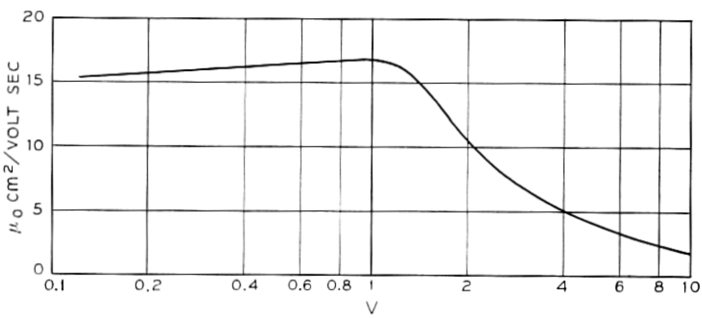

Fig. 6 — Theoretical mobility versus speed curve for H_3^+ in H_2, adopting the Langevin model. The speed has an adjustable scale factor which allows a horizontal shift without distortion of the curve shown.

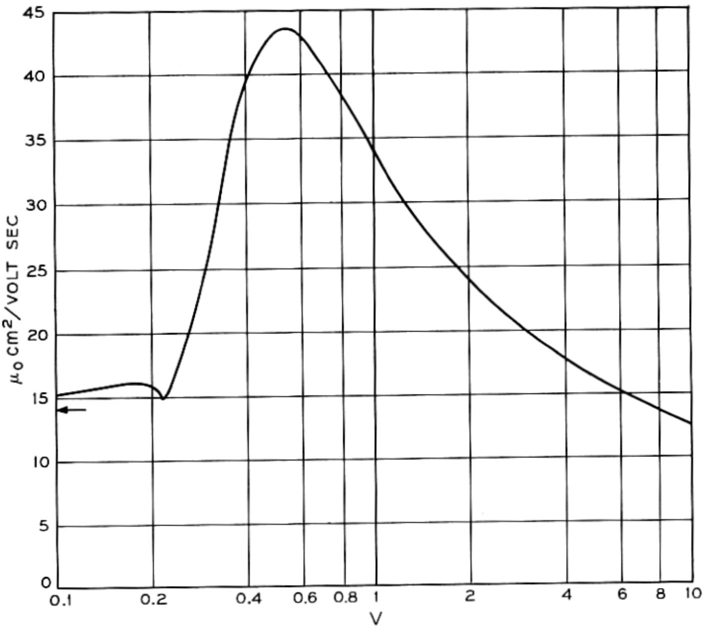

Fig. 7 — Theoretical mobility versus speed curve for H_3^+ in H_2, adopting a 4–6 potential model. The speed has an adjustable scale factor which allows a horizontal shift without distortion of the curve shown.

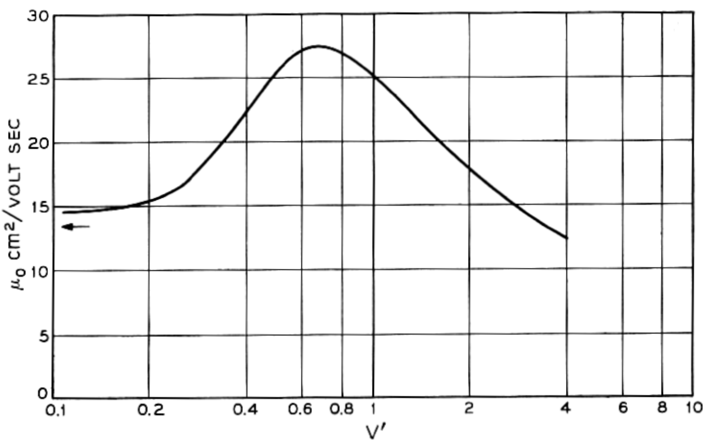

Fig. 8 — Theoretical mobility versus speed curve for H_3^+ in H_2, adopting a 4–8 potential model. Adaptation of results of Hershey.[5] V' is also a scaled speed. A horizontal shift without distortion of the curve shown is thus allowed.

hard sphere. Intermediate hardness yields an intermediate size bump. When we go on comparing these curves with the experimental curve shown in Fig. 5, we find the experimental bump in between the ninth power repulsion and the hard sphere. A Lennard-Jones type thirteenth power repulsion is thus quite a plausible candidate for a good fit.

We can make a further comparison between theory and experiment by identifying the velocities for which the maxima occur. The maxima in Fig. 6 and Fig. 7 occur roughly at $V = 1$, the experimental one at $v = 10^6$ cm/sec. We can thus use equation (3) to get an empirical value for the hard sphere radius a. We find

$$a = 1.7 \times 10^{-8} \text{ cm.}$$

Actually, the theoretical bump should be higher than the experimental one because the averaging process over velocities was omitted. Since the bump arises only for a restricted set of speeds it will be reduced by an averaging procedure.

The theoretical curves are not adjustable in a vertical direction and there is thus an unexplained discrepancy between theory and experiment in the low speed mobility value. The theoretical value results from the formula

$$\mu_0 = \frac{0.5105}{[\rho(\epsilon - 1)]^{\frac{1}{2}}} \left[1 + \frac{m(\text{gas})}{m(\text{ion})}\right]^{\frac{1}{2}} \frac{1}{300} \quad \text{cm}^2/\text{volt sec} \tag{13}$$

where ρ is the density and ϵ the dielectric constant of hydrogen. Taking for ρ the value 0.899×10^{-4} and for $\epsilon-1$ 2.73×10^{-4}, we find a value of 14.03 cm^2/volt sec for μ_0 while the measured one is 11.2. The cause for this discrepancy is not known at this time. It is possible that formula (13) is not quite correct for a molecular gas. The molecular polarizability is a tensor function which depends on orientation. The dielectric constant represents the polarizability response to a uniform field. If the ion is capable of orienting the molecules or comes so close as to experience details of molecular structure then the effective polarizability will be larger and the mobility smaller.

Before leaving the subject of comparison with experiment, I wish to call attention to the data of Ref. 9 taken at the very highest fields. A second rise of the mobility is indicated. The theory proposed cannot explain such a rise. If the explanation is right, this rise must be an experimental error or arise from a quite extraneous feature.

IV. CONCLUSIONS

It is the conclusion of this paper that the mobility bump which shows up in recent experiments is a normal feature of the classical theory of ionic mobility. It may actually be found in the classical papers on the subject[1,2,5] but the effect happens to be quite small for the Langevin model. The second model discussed here and the work of Hershey[5] show that it can be quite large, with the mobility rising to 300 percent of its polarization value. The size of the bump is critically dependent on the softness of the repulsive part of the potential. It is thus plausible to expect that a $1/r^{12}$ repulsion such as occurs in the Lennard-Jones potential will give rise to curves resembling the experimental ones. With calculations of this type one might set up a correspondence between "bump size" and "softness". However, a glance at the experimental data indicates that such an identification is not easy to make because the bump occurs primarily when either the ion or the molecule or both are extended systems. "Softness" may thus be an indirect attribute arising because the force is different for different orientations.

V. ACKNOWLEDGMENT

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