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An Empirical Relation between the Quenching Cross-sections of Metastable Argon and the Molecular Diameter of the Quenchers

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For polyatomic quenchers there is a fairly accurate linear relation between $\sigma_Q^{1/2}$ and r, where σ_Q is the quenching cross-section of rare gas metastables (especially $Ar(^3P_2)$) and r, the effective radius of the quencher.

The quenching process for metastable rare gas atoms by neutral molecules is one of the simplest and most elementary chemical reactions. So far many workers have studied the quenching cross-sections, σ_Q (esp. for metastable argon), and also discussed the quenching mechanism.[1–5)] However, as will be summarized in the next section, there seems to have been no definite conclusion as to the quenching mechanism. All the theoretical approaches are also unsuccessful.[6)] Therefore, what we should do first is to study the existing experimental data systematically and to search for empirical laws. As will be mentioned in the next section, some attempts of this kind have already been done, but the empirical laws they have proposed are not sufficiently quantitative.

The purpose of the present paper is to give a much more quantitative empirical law than has ever been reported: a linear relation between $\sigma_Q^{1/2}$ (esp. for metastable argon) and the effective diameter of the quencher. Empirical laws of this type for several gaseous processes have already been given in a previous paper.[7)] Our study shows that diatomic quenchers and polyatomic quenchers are rather clearly different. All the quenching cross-sections cited in this paper are those obtained from $k/\bar{v}$, where k is the rate constant and $\bar{v}$, the mean velocity of the colliding particles.

TABLE 1. THE QUENCHERS CONSIDERED IN THIS REPORT

Mono- and diatomic quenchers
1: Krypton, 2: Xenon, 3: Hydrogen, 4: Deuterium, 5: Nitrogen, 6: Carbon monoxide, 7: Nitrogen monoxide, 8: Oxygen, 9: Hydrogen chloride, 10: Hydrogen bromide, 11: Hydrogen iodide, 12: Chlorine, 13: Bromine, 14: Iodine monochloride,

Polyatomic quenchers
15: Water, 16: Ammonia, 17: Methane, 18: Dinitrogen oxide, 19: Carbon dioxide, 20: Methanol, 21: Acetylene, 22: Ethylene, 23: Ethane, 24: Acetaldehyde, 25: Hydrogen sulfide, 26: Nitrosyl chloride, 27: Chloromethane, 28: Carbonyl sulfide, 29: Sulfur dioxide, 30: Propane, 31: Propionaldehyde, 32: Isobutane, 33: Butane, 34: Benzene, 35: Carbon disulfide, 36: Dichloromethane, 37: 1-Butanol, 38: Phenol, 39: Bromomethane, 40: Pentane, 41: Toluene, 42: Benzaldehyde, 43: Chlorobenzene, 44: Chloroform, 45: *o*-Xylene, 46: *m*-Xylene, 47: *p*-Xylene, 48: 1-Hexanol, 49: *p*-Chlorotoluene, 50: 1-Naphthol, 51: 2-Naphthol, 52: Phosphorus trichloride, 53: *o*-Dichlorobenzene, 54: Carbon tetrachloride, 55: Iodomethane,

Fluorine-containing quenchers
56: Fluorine, 57: Nitrosyl fluoride, 58: Fluorine oxide, 59: Fluoromethane, 60: Nitrogen trifluoride, 61: Fluoroform, 62: Carbon tetrafluoride, 63: Trifluoromethoxy fluoride, 64: Dinitrogen tetrafluoride, 65: Thionyl fluoride, 66: Sulfur hexafluoride, 67: *p*-Fluorotoluene

Summary of the Present View on the Quenching Mechanism

Bourène and Calvé suggested that the ionization potential, I, is relevant to σ_Q from the fact that there is a rough inverse relation between σ_Q and I. As will be discussed later, this suggestion does not hold. Moreover, there is an experiment[8)] showing that the ionization process does not contribute to the quenching process of $Ar(^3P_2)$. Bourène and Calvé[3)] also suggested that the dispersion force is relevant and obtained a rough linear relation between σ_Q and the polarizability, α_Q, of the quencher. We reexamined this plot and obtained an approximate relation, $\sigma_Q \propto \alpha_Q^{2/3}$ (Fig. 1). However, if α_Q governs σ_Q, a dimensional analysis asserts that $\sigma_Q \propto \alpha_Q^{1/3}$. Hence, their second suggestion is also doubtful. Later we will see that the empirical relation just mentioned is one derivable from other empirical relations which appear more fundamental.

Setser *et al.*[1,2,8)] have been studying the quenching

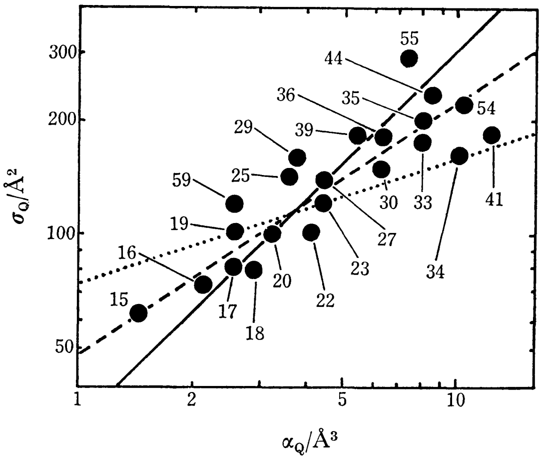

Fig. 1. The relation between σ_Q for $Ar(^3P_2)$ and the polarizability α_Q of quenchers. The slope of the lines are: ——1,– – – –2/3,······1/3. Thus the line with the slope 1/3 (which is suggested by a dimensional analysis or quantum mechanical considerations) does not fit the data, which are taken from Ref. 3. The line with the slope 2/3 best fits the data. The data for α_Q are taken from Ref. 11. All the numbers correspond to those in Table 1.

process extensively; they have also considered quenching mechanisms. Their conclusions thus far are summarized in Ref. 6. They plotted log σ_Q *vs.* log C_6, where C_6 is the van der Waals coefficient, and obtained a linear relation with a unit slope. Their experiments showed that the nature of the product channel is irrelevant to σ_Q. Therefore, they suggested that σ_Q is determined by the long-range forces in the entrance channel. Hereafter we will interpret the long-range interaction as the interaction which does not include the direct repulsive interaction due to the molecular core, *i.e.*, the overlap of electron clouds. As is the case of σ_Q *vs.* α_Q, however, the slope of the log σ_Q *vs.* log C_6 plot apparently contradicts the mechanism suggested (a dimensional analysis shows $\sigma_Q \propto C_6^{1/3}$). King and Setser[6] suggested that this contradiction is either because the long-range forces are not properly represented by C_6, or because the probability of quenching increases in a systematic way, making the slope larger than 1/3. Thus, they seem to assert that the relevant mechanism is due to long-range interactions (esp. dipole-dipole interaction). However, apart from the *ad hoc* nature of their explanation of the value of the slope, the long-range-force mechanism contradicts the facts that σ_Q for Ar($^3P_2$) and that for Ar($^1P_1$) have the same order of magnitude and that permanent dipoles are irrelevant to σ_Q, as will be shown below (Fig. 6).

Thus, we may conclude that there is no conclusive view on the quenching mechanism of metastable rare gas atoms.

Phenomenological Survey of the Quenching Process

As was discussed in the introductory part of this paper, the $\sigma_Q \propto \alpha_Q^x$ ($x \approx 2/3$) and $\sigma_Q \propto C_6^y$ ($y \approx 1$) relations afford universal phenomenological relations independent of the detailed nature of the quenchers. However, these relations are not sufficiently quantitative.

It has been shown[7] that the effective hard-core radius of the molecule, r, appearing in the statistical mechanics of liquids can be successfully used as the representative length of the molecules in gaseous reactions. Therefore, it is natural to try to find the relation between r and σ_Q. It is known that r is a good measure of the radius of the repulsive core of molecules, *i.e.*, a good measure of the effective radius of the electron cloud of molecules. A dimensional analysis suggests a linear relation between $\sigma_Q^{1/2}$ and r. As a convenient measure of r, we adopted $r_w = (3V_w/4\pi N)^{1/3}$, where V_w is the van der Waals volume of the quencher, which is calculated by using the tables of Bondi,[9] and N, the Avogadro constant. A linear relation holds between r and r_w, as has been shown in Ref. 10. First, we will consider Ar($^3P_2$).

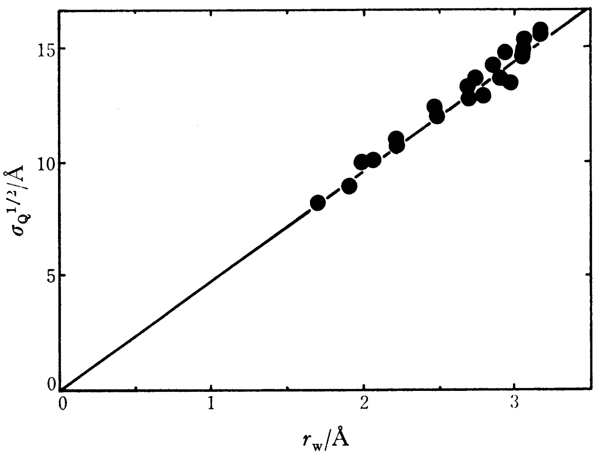

Fig. 2. The linear relation between r_w (see the text) and $\sigma_Q^{1/2}$ for polyatomic quenchers consisting of atoms belonging to the first and second periods of the periodic table. The data are taken from Ref. 4.

Figure 2 shows the linear relation for polyatomic molecules involving only atoms belonging to the first and second periods of the periodic table. The linear relation is much more accurate than any previously reported. Note that the plot is not a log-log one, in contrast to the relations previously obtained. This linear relation, however, does not hold accurately for quenchers containing sulfur, bromine, *etc.* Still, we can get a universal linear law similar to it. For this purpose we systematically modify the van der Waals volumes allotted to the larger atoms as follows: for the atoms belonging to the $(n+2)$-th ($n>0$) period of the periodic table, the modified van der Waals volume, V_w', is related to that of Bondi[9] as $V_w' = (1.7)^n V_w$. This modification seems to reflect the extension of the outermost shell of atoms, but we cannot give a clear physical meaning for it. At any rate, by this modification of the van der Waals volume allotted to the larger atoms, we get the linear relation shown in Fig. 3 for all polyatomic quenchers except those containing fluorin atoms. The accuracy of the linear relation is excellent. The effect of the modification of the van der Waals volumes is shown in Fig. 4. As may clearly be seen from Fig. 5, the diatomic quenchers and the polyatomic quenchers

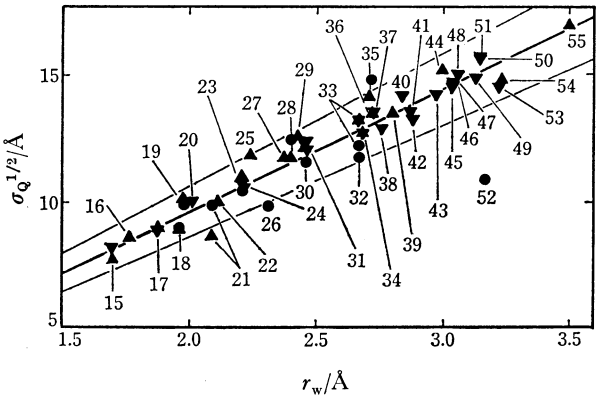

Fig. 3. The linear relation between r_w and $\sigma_Q^{1/2}$. r_w is calculated from the modified van der Waals volumes in the text. The line denotes $\sigma_Q^{1/2} = 4.80\,r_w$. The thin lines show $\sigma_Q^{1/2} = (4.80 \pm 0.48)\,r_w$. Thus our empirical relation is very accurate than those so far obtained. All the numbers in the figure correspond to those in Table 1. The data are taken from Refs. 1, 2 (●), Ref. 3 (▲), and Ref. 4 (▼). The quenchers containing fluorine atoms deviate from the linear law wildly. This suggests that the quenching mechanism for these compounds are different from other quenchers.

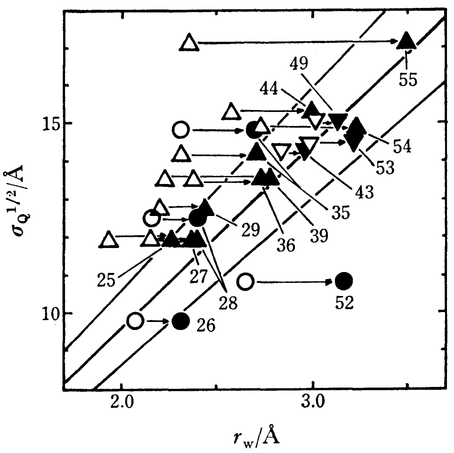

Fig. 4. The effect of the modification of the van der Waals volumes. Open symbols show the $\sigma_Q^{1/2}$ *vs.* r_w relation before the modification of the van der Waals volumes and solid symbols show that after the modification. All the numbers correspond to those in Table 1. Triangles and circles correspond to those in Fig. 3.

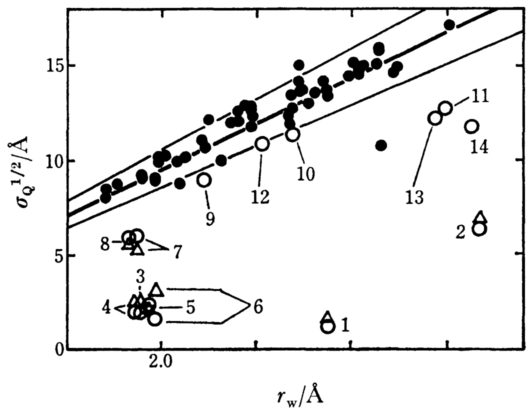

Fig. 5. The $\sigma_Q^{1/2}$ *vs.* r_w relation for mono- and diatomic quenchers. The σ_Q of these quenchers are systematically smaller than those of polyatomic quenchers (denoted by solid symbols). All the numbers correspond to those in Table 1.

TABLE 2. IRRELEVANCE OF THE POLARIZABILITY α_Q (Å^3) TO WHETHER OR NOT $\sigma_Q^{1/2} \propto r_w$ HOLDS

Although King and Setser[6)] suggested that the quenchers with smaller α_Q values are different from other quenchers, their suggestion does not hold. In the table, the numbers in parentheses show the α_Q values in Å^3.

Mono- and diatomic quenchers		Polyatomic quenchers	
O_2	(1.57)		
N_2	(1.74)	H_2O	(1.45)
NO	(1.70)		
CO	(1.94)	NH_3	(2.16)
Kr	(2.48)	CO_2	(2.59)
HCl	(2.58)	CH_4	(2.56)
HBr	(3.49)	H_2S	(3.61)
		SO_2	(3.78)
		CH_3OH	(3.25)

are different. This difference could not be found, though, as long as we had only the rough empirical laws mentioned above.

The difference cannot be ascribed to that of the number of (valence) electrons nor to that of the ionization potential (see also the next section). Furthermore, although the magnitude of the polarizability may seem relevant, as has been suggested by Setser *et al.*, α_Q has no direct effect on whether $\sigma_Q^{1/2} \propto r$ holds or not (Table 2). Therefore, in so far as we base our conclusions on the existing data, the most natural conclusion is that the number of nuclei in the quencher is relevant to the quenching process (mechanism). This further suggests that the number of vibrational degrees of freedom of the quencher is relevant.

Irrelevance of Other Quantities

The irrelevance of other quantities, such as the permanent dipole moment, the ionization potential, *etc.*, to the quenching mechanism can be seen as follows. Possible relevant quantities, other than r, may include the reduced mass, μ, of colliding particles; the de Broglie wave length, λ; the permanent dipole moment, D; the ionization potential, I; the initial relative velocity, $v(=(3kT/\mu)^{1/2})$, and the initial kinetic energy, $E(=3kT/2)$. A dimensional analysis implies the following functional relation:

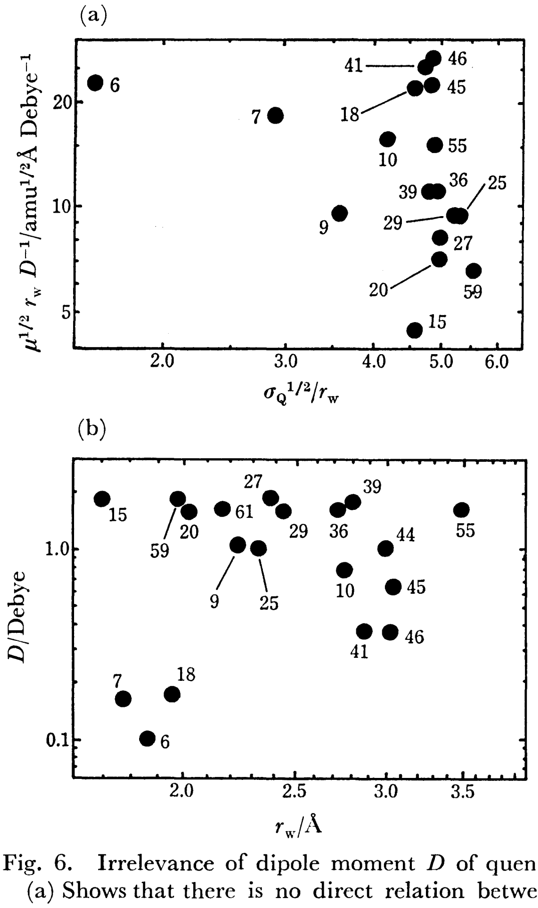

Fig. 6. Irrelevance of dipole moment D of quenchers. (a) Shows that there is no direct relation between D and σ_Q. (b) Shows, furthermore, that D is irrelevant to r_w. Therefore there is no indirect relation between D and σ_Q either.

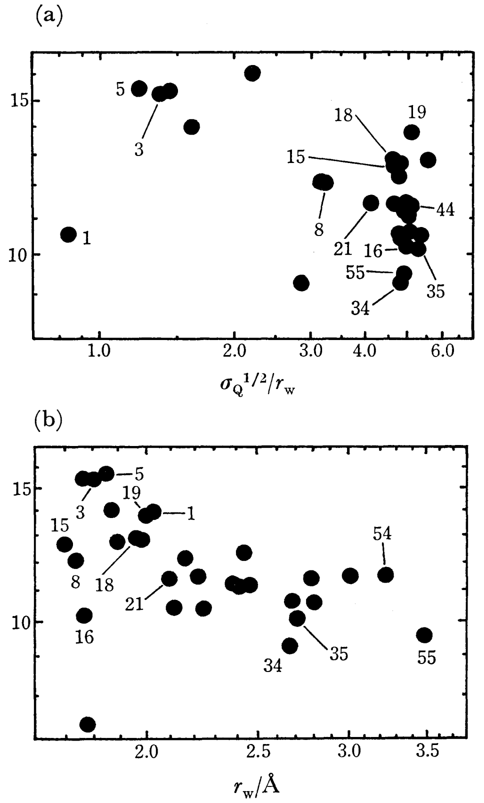

Fig. 7. Irrelevance of the ionization potential I of quenchers. (a) Shows that there is no direct relation between I and σ_Q. Although (b) shows a vague correlation between r_w and I (this is the reason why Bourène and Calvé suggested the relevance of I), but (a) and (b) show that I is substantially irrelevant to σ_Q. All the numbers correspond to those in Table 1. The data for I are taken from Ref. 2.

$$\sigma_Q^{1/2} = rf(\lambda/r,\, I,\, D^{1/2}/\mu^{1/2}r,\, \cdots)$$

where constant dimensional quantities are suppressed. All the existing data are obtained from experiments performed under almost the same E (or T). Figures 6—8 show that all the quantities other than r have no direct relevance to σ_Q. The irrelevance of the permanent dipole moment is evidence that the interaction due to the so-called long-range forces has no direct effect on σ_Q, as we suggested at the beginning of this paper.

Discussion

It may seem quite curious that the number of nuclei in the quencher is relevant. There is a possibility that the relevance is explained by the relation between the stochasticity of the motion of a nonlinear oscillator and its number of degrees of freedom. The stochasticity of the internal motion of the quencher enhances its quenching ability. Diatomic quenchers never exhibit stochastic internal motion, so that the quenching cross-section is smaller than would be expected from the empirical law for polyatomic molecules. This explanation is mere speculation, but it is fascinating because there is a growing interest in the chaos appearing in dynamical systems with even a small number of degrees of freedom.

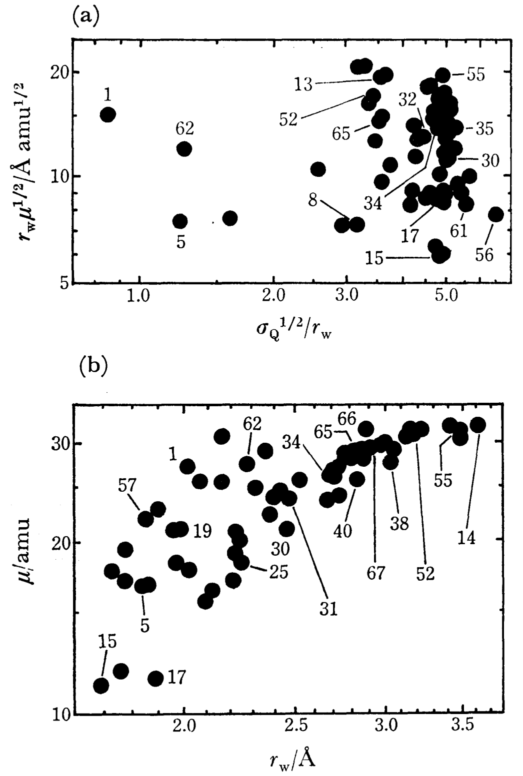

Fig. 8. Irrelevance of the reduced mass μ or the de Broglie wavelength of quenchers. (a) Shows that there is no direct relation between μ and σ_Q. Of course, as is shown in (b), there is a positive correlation between μ and r_w, but the comparison of the scattered distribution of points in (b) and fairly compact distribution of points in (a) implies that reduced mass (and de Broglie wave length) are irrelevant to σ_Q. All the numbers correspond to those in Table 1.

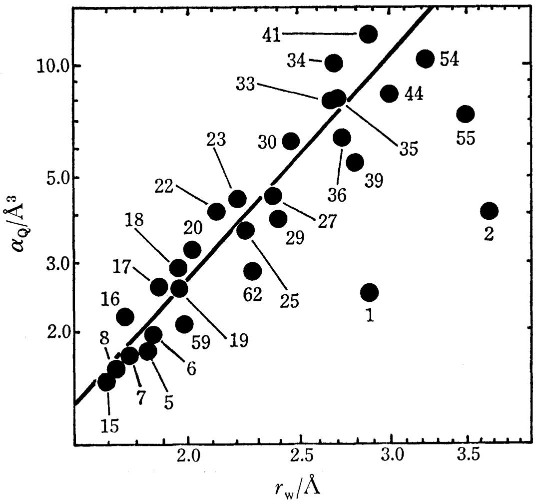

Fig. 9. The relation between modified r_w and the polarizability α_Q. The slope of the line is 3, *i.e.*, $\alpha_Q \propto r_w^3$. α_Q are taken from Ref. 11. All the numbers correspond to those in Table 1.

A close examination of σ_Q suggests that there is some effect of the shape of the quencher. For the series of quenchers with the same van der Waals volume, we have the order of: butane>isobutane and *p*-xylene>

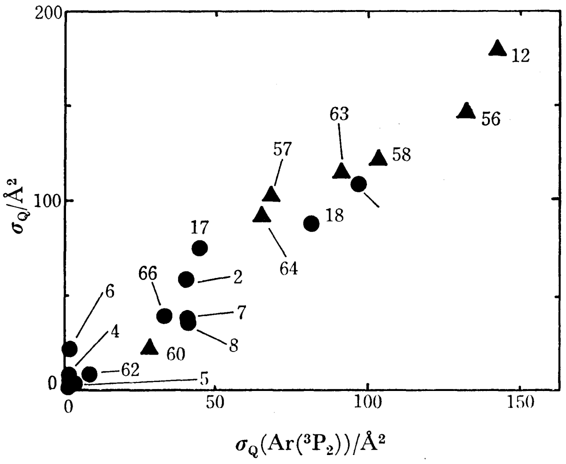

Fig. 10. The relation between the quenching cross sections of Ar($^3P_2$) and Ar($^3P_0$)[1] (●) or Kr ($^3P_2$)[2] (▲). All the numbers correspond to those in Table 1.

m-xylene>*o*-xylene. Thus, the deviation from the spherical shape increases σ_Q slightly. These deviations are, however, very small, and the main feature is that σ_Q is governed by the effective radius of the quencher.

The empirical relation, $\sigma_Q \propto \alpha_Q^{2/3}$, mentioned earlier is derived from $\sigma_Q^{1/2} \propto r_w$ and the empirical relation $\alpha_Q \propto r_w^3$ shown in Fig. 9.

Figure 10 suggests that the quenching mechanisms for Ar($^3P_2$) and Ar($^3P_0$) or Kr($^3P_2$) are the same. However, since only a few results are known for Kr($^3P_2$) for polyatomic quenchers, we cannot make a $\sigma_Q^{1/2}$ *vs.* r_w plot. It seems that the same conclusion can be drawn for Xe($^3P_2$), but there are not sufficient data in this case, either. For He(2^1S), as was shown in a previous paper,[7] no universal relation between σ_Q and r was found.

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